

STATES OF MATTER

- Matter exists in three distinct physical states: gas, liquid and solid. By definition matter is anything which has mass and occupies space.
- Solids under ordinary conditions have definite volume and shape, and tend to maintain these even under deforming forces.
- Liquids have no definite volume but take the shape of the vessel into which they are poured.
- Gases on the other hand maintain neither volume nor the shape, and completely fill the container in which they are introduced. Gases can be expanded and compressed very easily.
- In this subtopic the following aspects should be discussed.
 - Gaseous state
 - Liquid state

1. GASEOUS STATE

- This is a simplest state of matter. Let us now focus our attention on the behavior of substances which exist in the gaseous state under normal conditions of temperature and pressure.
- A look at the periodic table shows that only eleven elements exist as gases under normal conditions.

i.e.

Group Number	I	V	VI	VII	VIII
	H				He
		N	O	F	Ne
				Cl	Ar
					Kr
					Xe
					Rn

- The gaseous state is characterized by the following properties: -
 - Gaseous are highly compressible.

- Gases exert pressure equally in all the directions.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases have much lower density than liquids and solids.
- Gases expand appreciably on heating.

MEASURABLE PROPERTIES OF GASES

The behavior of gases can be described in terms of certain parameters. These are described here below.

1. VOLUME

- Gases fill the container in which they are placed. So the volume of gas is equal to that of its container. Volume can be expressed in litre (L), millilitre (ml), or cubic centimeter (cm^3).
- The SI unit of volume is cubic meter (m^3). However smaller units such as dm^3 and cm^3 are more frequently employed. These are related to each other as;

$$1\text{m}^3 = 10^3\text{dm}^3 = 10^6\text{cm}^3$$

Furthermore,

$$1\text{L} = 1\text{dm}^3$$

$$1\text{ml} = 1\text{cm}^3$$

2. PRESSURE

- Pressure is the force per unit area. Gases exert pressure uniformly in all the directions.
- In the laboratory atmospheric pressure is measured with the help of a Barometer.
- A standard pressure of one atmosphere (1 atm) is defined as the pressure exerted by exactly 760 mm of mercury column at 0°C .
- The SI unit of pressure is Pascal (Pa). It is defined as the pressure exerted when a

force of 1 Newton (N) acts upon an area equal to 1m^2 .

- Pascal relates to other units by the relation,

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

Furthermore,

$$1 \text{ atm} = 760 \text{ torr} = 760\text{mmHg} = 101325 \text{ Nm}^{-2}(\text{Pa})$$

3. TEMPERATURE

- Temperature is a measure of degree of hotness. In gases It is a measure of kinetic energy possessed by the molecule.
- Instrument used to measure temperature of any substance is called thermometer.

Temperature scale mostly used in the scientific work is the Celsius scale formerly known as **centigrade scale**.

The value of 0°C has been accepted as the standard temperature as per International agreement.

Temperatures are also expressed on the Kelvin scale, whose zero corresponds to -273.15°C . Thus $T(\text{K}) = 273.15 + ^\circ\text{C}$.

- Normal temperature and pressure (NTP) is the temperature of 0°C or (273.15K) and pressure is equal to 1 atm or $(760\text{mmHg} = 1.01325 \times 10^5\text{Pa})$ is sometimes known as Standard Temperature and Pressure (S.T.P.).

GAS LAWS

- Gas laws are generalizations which regards the macroscopic behaviour of gaseous substances in terms of volume, temperature and pressure.

These include:-

- ♦ Boyle's law
- ♦ Charles law
- ♦ Avogadro's law
- ♦ Dalton's law of partial pressure

1. BOYLE'S LAW

(Pressure volume relationship 1662)

- Boyle's law states that "**The volume of a fixed amount of gas at a constant temperature is inversely proportional to the pressure exerted on it**"

- Then if V is the volume of a gas and P is the pressure of that gas at a fixed temperature, then Boyle's law can be expressed mathematically as

$$V \propto 1/P$$

$$\text{Or, } PV = K$$

- Consider a given amount of a gas occupying a volume V_1 under a pressure P_1 , then from Boyle's law,

$$P_1V_1 = K$$

- Now if temperature is kept constant and pressure is changed to P_2 , so that volume change to V_2 then from Boyle's law,

$$P_2V_2 = K$$

Hence

$$P_1V_1 = P_2V_2$$

Where

P_1 = Original pressure

V_1 = Original volume

P_2 = New pressure

V_2 = New volume

- Thus when a gas is allowed to expand (or is compressed) at constant temperature from an initial volume of V_1 to a final volume of V_2 , the final pressure P_2 can be calculated so long as the initial pressure P_1 is known.

GRAPHICAL REPRESENTATION OF BOYLE'S LAW

- Boyle's law can be expressed graphically as:

(a) $V \text{ vs } P$

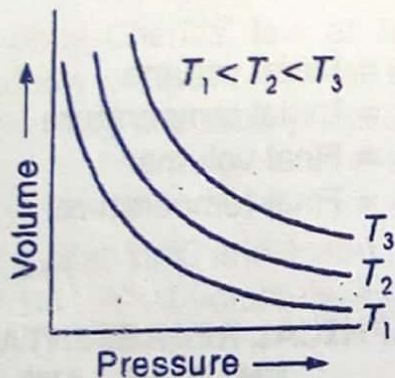
(b) $V \text{ vs } 1/P$

(c) $PV \text{ vs } P$

(a) VOLUME - PRESSURE GRAPH

- When the volume (V) of a certain amount of a gas at any fixed temperature is plotted against pressure (P) a hyperbolic curve is obtained.
- The hyperbolic curve obtained when volume (V) of a gas is plotted against pressure (P) at any constant temperature is called **volume - pressure isotherm**.

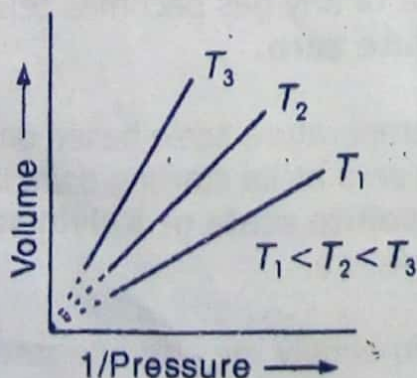
Nature of the graph



(a) VOLUME - 1/PRESSURE GRAPH

- When volume (V) of a fixed amount of a gas at any constant temperature is plotted against reciprocal of pressure ($1/p$), a straight line plot passing through the origin is obtained.

Nature of the graph



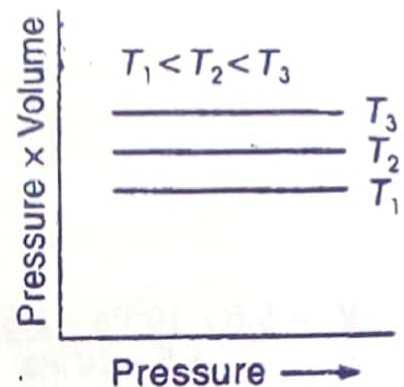
(c) PRESSURE X VOLUME Vs PRESSURE GRAPH

- When the product of pressure and volume (PV) for a certain amount of a gas at a constant temperature is plotted against pressure (P) the isotherm is a straight line parallel to the pressure axis.
- Thus the PV value remain constant at all

the pressures.

- At any pressure, the value of the product PV increases with increase in temperature.

Nature of the graph



Problem 1:

An inflated helium balloon with a volume of 0.55 L at 1 atm is allowed to rise to a height of 6.5 km, where the pressure is about 0.4 atm. Assuming that the temperature remains constant, what is the final volume of the balloon?

Solution

Data

$$\begin{aligned} P_1 &= 1 \text{ atm} \\ P_2 &= 0.4 \text{ atm} \\ V_1 &= 0.55 \text{ L} \\ V_2 &= ? \end{aligned}$$

From

$$P_1 V_1 = P_2 V_2$$

$$\text{Then } V_2 = \frac{P_1 V_1}{P_2}$$

$$V_2 = \frac{1 \times 0.55 \text{ atm. L}}{0.4 \text{ atm}}$$

$$V_2 = 1.4 \text{ L}$$

Problem 2:

A gaseous SO_2 at a pressure of $5.6 \times 10^3 \text{ Pa}$ occupies the volume of 1.53 L. If the pressure is changed to $1.5 \times 10^4 \text{ Pa}$ at a constant temperature, what will be the new volume of the gas?

Data

$$\begin{aligned}P_1 &= 5.6 \times 10^3 \text{ Pa} \\V_1 &= 1.53 \text{ L} \\P_2 &= 1.5 \times 10^4 \text{ Pa} \\V_2 &= ?\end{aligned}$$

From Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2}$$

$$V_2 = \frac{5.6 \times 10^3 \text{ Pa} \times 1.53 \text{ L}}{1.5 \times 10^4 \text{ Pa}}$$

$$V_2 = 0.57 \text{ L}$$

2. CHARLES' LAW

(Volume - Temp relationship)

- Charles' (1787) and later Gay - Lussac (1808) observed that if the pressure is kept constant the volume of a certain amount of a gas changes linearly with temperature.
- Generally Charles' law states that **"Volume of a fixed amount of a gas is directly proportional to the absolute temperature at constant pressure"**

Mathematically

$$V \propto T \text{ (constant } P)$$

On removing proportionality sign.

$$V = KT$$

$$\text{Or } \frac{V}{T} = K$$

- Consider certain amount of a gas at temperature T_1 under constant pressure so that its volume be V_1 . According to Charles' law.

$$\frac{V_1}{T_1} = \text{Constant}$$

Now if pressure is kept constant and

temperature is changed to T_2 when the volume changes to V_2 then,

$$\frac{V_2}{T_2} = \text{Constant}$$

- Since the amount of gas and pressure remains unchanged, hence;

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where

V_1 = Initial volume

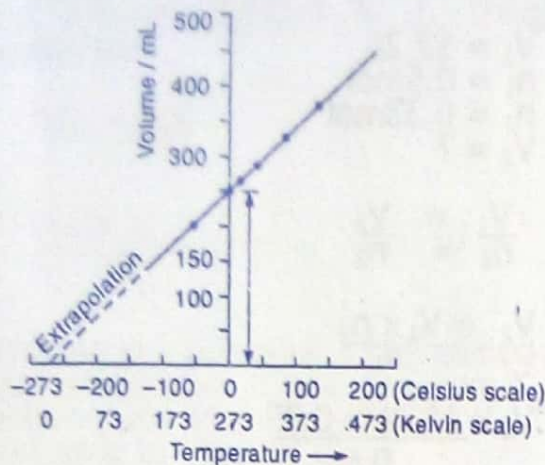
T_1 = Initial temperature

V_2 = Final volume

T_2 = Final temperature

GRAPHICAL REPRESENTATION OF CHARLES LAW

- Observation showed that the volume of any gas would be zero at a temperature of -273.15°C . Then -273.15°C was taken as a new starting temperature scale called **Kelvin**.
- The lowest temperature of -273.15°C which gas ceases to exist or at which volume of any gas becomes zero is called **absolute zero**.
- The temperature scale based on the absolute zero as its starting point is known as **absolute scale or Kelvin scale** of temperature.
- Experimentally the absolute zero (zero of Kelvin scale) can be obtained by plotting a graph of volume of a certain amount of gas against temperature on the **Celsius scale** and extrapolating such straight line plot as shown below.



NB: Gases obey Charles' law at high temperature and low pressure. But fail to obey it at low temperature and high pressure.

Problem 3:

A sample of gas at 15°C and 1 atm has a volume of 2.58L. What volume will this gas occupy at 38°C and 1 atm?

Solution

Since temperature changes but pressure remains constant, then Charles' law applies.

Data

$$T_1 = 15 + 273K$$

$$T_2 = 38 + 273K$$

$$V_1 = 2.58L$$

$$V_2 = ?$$

$$\text{From } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{T_2 V_1}{T_1}$$

$$V_2 = \frac{311 \times 2.58 \text{ K.L}}{288K}$$

$$V_2 = 2.79L$$

NB: The new volume is greater than the initial volume which makes physical sense because the gas will expand as it is heated.

Problem 4.

Certain amount of a gas occupies a volume of 400ml at 17°C. To what temperature

should it be heated so that its volume gets
(i) Doubled
(ii) Reduced to half?

Solution

(i) Data

$$V_1 = 400ml$$

$$T_1 = 17 + 273.15 = 290.15K$$

$$V_2 = 2 \times 400 = 800ml$$

$$T_2 = ?$$

From Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = \frac{T_1 V_2}{V_1}$$

$$= \frac{800 \times 290.15}{400}$$

$$= 580.3K$$

(ii) Data

$$V_1 = 400ml$$

$$T_1 = 290K$$

$$V_2 = \frac{1}{2} \times 400 = 200ml$$

$$T_2 = ?$$

From Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = \frac{T_1 V_2}{V_1}$$

$$T_2 = \frac{290.15 \times 200}{400}$$

$$T_2 = 145.07K$$

3. AVOGADRO'S LAW

- Amedeo Avogadro (1811) assuming that the atoms in all gases (except noble gases) did not exist singly but in a divisible group called molecule, proposed the law called **Avogadro's law**.
- Avogadro's law states that "**For a gas at constant temperature and pressure, the volume is directly proportional**

P_2 temperature being held constant at T_1 and volume changed to V . Then from Boyle's law.

$$P_1 V_1 = P_2 V$$

Or

$$V = \frac{P_1 V_1}{P_2} \dots\dots\dots (i)$$

- Now assume pressure is maintained at P_2 and temperature is changed from T_1 to T_2 while volume change from V to V_2 . Then according to Charles' law.

$$\frac{V}{T_1} = \frac{V_2}{T_2}$$

Or $V = \frac{V_2 \times T_1}{T_2} \dots\dots\dots (ii)$

Equating the value of V from equations above one can write,

$$\frac{P_1 V_1}{P_2} = \frac{V_2 T_1}{T_2}$$

Or

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Combined gas equation or general equation of a gas.

Problem 7.

For each of the following statements indicate how the final volume (V_f) is related to the initial volume (V_i), for a fixed amount of gas.

- (i) The pressure is decreased from 3atm to 1atm while the temperature is held at 5° C.
- (ii) The temperature is lowered from 400K to 100K while the pressure is held constant at 1atm.
- (iii) The temperature is raised from 200K to 300K while the pressure is increased from 2atm to 3atm.

Solution

- (i) Since pressure changes but temperature is kept constant then Boyle's law applies,

i.e. $P_i V_i = P_f V_f$

Or

$$V_f = \frac{P_i V_i}{P_f}$$

$$V_f = \frac{3 \times V_i}{1}$$

$$V_f = 3V_i$$

Then final volume relates to initial volume such that V_f is three times V_i .

- (ii) Since temperature changes but pressure remains constant then Charles' law applies,

i.e. $\frac{V_i}{T_i} = \frac{V_f}{T_f}$

Or $V_f = \frac{T_f \times V_i}{T_i}$

$$V_f = \frac{100 V_i}{400}$$

Then V_f relates to V_i such that V_f is 0.25 times V_i .

- (iii) Since there is simultaneous change of P and T then we use the combined gas equation to find the relation.

i.e. $\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$

Or

$$V_f = \frac{P_i \times T_f \times V_i}{P_f \times T_i}$$

$$V_f = \frac{2 \times 300 V_i}{3 \times 200}$$

$$V_f = V_i$$

Then V_f relates to V_i such that V_f is equal to V_i .

Problem 8.

Volume of a certain amount of a gas at 27° C and $1.014 \times 10^5 \text{ Nm}^{-2}$ pressure is 30m^3 . What would be the change in volume of the gas if the temperature is raised to 35° C, and pressure to $1.72 \times 10^5 \text{ Nm}^{-2}$?

Solution

- Since the pressure and temperature are

changing we use the combined gas equation to find the final volume.

om,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

here,

$$P_1 = 1.0414 \times 10^5 \text{ Nm}^{-2}$$

$$V_1 = 30 \text{ M}^3$$

$$T_1 = 300 \text{ K}$$

$$P_2 = 1.72 \times 10^5 \text{ Nm}^{-2}$$

$$V_2 = ?$$

$$T_2 = 308 \text{ K}$$

Then we can write

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{1.014 \times 10^5 \times 30 \times 308}{1.72 \times 10^5 \times 300}$$

$$V_2 = 18.15 \text{ m}^3$$

Then change in volume

$$\Delta V = V_2 - V_1$$

$$= 18.15 - 30$$

$$= -11.84 \text{ M}^3$$

The negative sign means that there is a decrease in volume. Thus the volume decreased by 11.84 m^3

Problem 9

A certain amount of a gas at 25°C and a pressure of 0.8 atm is contained in a glass vessel. Suppose that the vessel can stand a pressure of 2 atm . How high can you raise the temperature of the gas without bursting the vessel.

Solution

From,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Since in glass vessel no expansion of volume, then $V_1 = V_2$

Then

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Where

$$P_1 = 0.8 \text{ atm}$$

$$T_1 = 25^\circ\text{C} + 273$$

$$P_2 = 2 \text{ atm}$$

$$T_2 = ?$$

We have from above

$$0.8 \text{ atm} = 2 \text{ atm}$$

$$298 \text{ K} \quad T_2$$

$$T_2 = \frac{298 \text{ K} \times 2 \text{ atm}}{0.8 \text{ atm}}$$

$$T_2 = 745 \text{ K}$$

Then temperature can be raised to 745 K .

IDEAL GAS EQUATION

Gases obeying the Boyle's and Charles' law are formed as ideal gases. A mathematical expression describing the simultaneous effect of the changes in temperature and pressure on the volume of a given amount of a gas, is called **ideal gas equation**.

- Ideal gas equation can be derived from Boyle's, Charles and Avogadro's law.

i.e.

$$V \propto \frac{1}{P} \text{ (constant } T) \dots\dots\dots\text{(i) Boyle's law}$$

$$V \propto T \text{ (Constant } P) \dots\dots\dots\text{(ii) Charles' law}$$

$$V \propto n \text{ (Constant } P \text{ and } T) \dots\dots\dots\text{(iii) Avogadro's law}$$

- Combining the three above equations we get,

$$V \propto \frac{n \cdot T}{P}$$

- The proportionality sign above can be converted to equality as follows.

$$V = \frac{K \cdot n \cdot T}{P}$$

Or

$$PV = n \cdot K \cdot T \dots\dots\dots\text{(iv)}$$

- Where K is proportionality constant, which is found to be independent of the nature of the gas and for this case is called universal gas constant, denoted by the letter R .

- The equation (iv) above becomes,

$$PV = nRT$$

Ideal gas equation

NB: For one mole of a gas $n = 1$, then ideal gas equation becomes,

$$PV = RT$$

CALCULATION OF DENSITY FROM IDEAL GAS

- Ideal gas equation is used to get the density of a gas.

Recall

$$PV = nRT$$

But

$$\text{Number of moles} = \frac{\text{mass}}{\text{Molar mass}}$$

$$PV = \frac{mRT}{M_r}$$

Or

$$P = \frac{m \cdot R \cdot T}{V \cdot M_r}$$

$$P = \frac{\rho RT}{M_r} \text{ Since } \frac{m}{V} = \rho$$

Or

$$\rho = \frac{PM_r}{RT}$$

UNIVERSAL GAS CONSTANT (R)

- The constant R in the ideal gas equation, $PV = nR$ is commonly known as the Universal gas constant.

From

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

- Now we know that,

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{length})^2}$$

Also volume = (length)³

Therefore,

$$R = \frac{\text{Force} \times (\text{length})^3}{(\text{Length})^2 \times \text{No. of moles} \times \text{Temp}}$$

$$R = \frac{\text{Force} \times \text{length}}{\text{No. of moles} \times \text{Temp}}$$

$$R = \frac{\text{Work}}{\text{No. of moles} \times \text{Temp.}}$$

- Thus, the universal gas constant is a measure of energy change (work done) per mole of the gas for one degree change in its temperature.

NUMERICAL VALUE OF R

- To get the real value of R consider ideal gas equation,

$$PV = nRT$$

Make R the subject,

$$R = \frac{PV}{nT}$$

- The magnitude and unit of R depends upon the units in which pressure, volume and temperature are expressed at S.T.P

- When pressure is expressed in atmosphere and volume in dm³

$$P = 1 \text{ atm}$$

$$V = 22.4 \text{ dm}^3$$

$$T = 273 \text{ K}$$

$$R = ?$$

Then from,

$$R = \frac{PV}{nT}$$

$$R = \frac{1 \times 22.4 \text{ atm} \cdot \text{dm}^3}{1 \times 273 \text{ mol} \cdot \text{K}}$$

$$R = 0.0821 \text{ atm} \cdot \text{dm}^3 \text{ Mol}^{-1} \text{K}^{-1}$$

EXAMPLE OF PROBLEMS ON

IDEAL GASES.

Qn 10. Necta 1992 May P^I Qn 2c
Calculate the density of oxygen gas at 298 K and 0.988 atm.

Solution**Data**

$$\begin{aligned} T &= 298\text{K} \\ P &= 0.988\text{atm} \\ M_r &= 32\text{gmol}^{-1} \end{aligned}$$

From ideal gas equation,

$$\begin{aligned} PV &= nRT \\ \text{But } n &= \frac{m}{M_r} \end{aligned}$$

Then,

$$PV = \frac{mRT}{M_r}$$

$$P = \frac{mRT}{VM_r}$$

$$\text{But } \frac{m}{V} = \text{density } (\rho)$$

$$P = \frac{\rho RT}{M_r}$$

$$\rho = \frac{PM_r}{RT}$$

$$\rho = \frac{0.988 \times 32 \text{ atm. gmol}^{-1}}{0.0821 \times 298 \text{ atm.dm}^3 \text{ Mol}^{-1} \text{ K}^{-1} \text{ K}}$$

$$\rho = 1.29\text{g/dm}^3$$

Qn 11 Necta May 1996 P^I Qn 2c and d.

(c) A 2.0g sample of water is vaporized completely into a 10L container at 200°C. Calculate the pressure of water vapor in this container at 200°C.

(d) Calculate the molecular weight of a gas if 1.82g of the gas occupies a volume of 2L at 25°C and 737 mmHg. Assume the gas behaves ideally.

Solution

(c) Required pressure

Data

$$\begin{aligned} m &= 2\text{g} \\ V &= 10\text{L} \\ T &= 200 + 273\text{K} \\ M_r &= 18\text{gmol}^{-1} \end{aligned}$$

From ideal gas equation,

$$\begin{aligned} PV &= nRT \\ PV &= \frac{mRT}{M_r.V} \end{aligned}$$

$$P = \frac{2\text{g} \times 0.0821\text{atm.dm}^3 \text{ Mol}^{-1} \text{ K}^{-1} \cdot 473\text{K}}{18\text{gmol}^{-1} \times 10\text{dm}^3}$$

$$P = 0.43\text{atm.}$$

Therefore pressure of water vapor in the container is 0.43 atm.

(d) Required: Molecular weight

Data

$$\begin{aligned} m &= 75\text{g} \\ V &= 1\text{L} \\ P &= 4.02\text{atm} \\ T &= (100 + 273)\text{K} \end{aligned}$$

From,

$$\begin{aligned} PV &= nRT \\ PV &= \frac{mRT}{M_r} \end{aligned}$$

$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{75\text{g} \times 0.0821\text{atm.dm}^3 \text{ Mol}^{-1} \text{ K}^{-1} \times 373\text{K}}{4.02\text{atm} \times 1\text{dm}^3}$$

$$M_r = 571\text{gmol}^{-1}$$

Qn 12. Necta 2000 P^I Qn3

(a) State

- (i) Boyles' law
- (ii) Charles' law

(iii) Avogadro's law

(b) SO_2 used in the manufacture of sulphuric acid is obtained from sulphide ore;-



Find the mass of oxygen in grams reacting when 75 liters of SO_2 are produced at 100°C and 1.04 atm

Solution:

(b) Required: Mass of oxygen in grams
Data for SO_2

$$V = 75\text{L}$$

$$T = (100 + 273)\text{K}$$

$$P = 1.04\text{atm}$$

1st case:

Use the ideal gas equation to find the number of moles of SO_2

From

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{1.04 \times 75}{0.0821 \times 373}$$

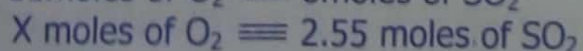
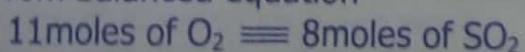
$$n = 2.55\text{moles}$$

2nd case:

Find number of moles of oxygen used in the reaction by comparing them in balanced equations

i.e.

From balanced equation



$$n_{\text{O}_2} = \frac{11 \times 2.55}{8}$$

$$n_{\text{O}_2} = 3.5\text{ moles}$$

$$\text{But number of moles} = \frac{\text{mass}}{\text{Molar mass}}$$

$$\text{Then mass} = n \times M_r$$

$$= 3.5 \times 32 \times \text{gmol}^{-1} \times \text{mol}$$

$$= 112\text{g}$$

Then mass of oxygen reacting is 112g.

Qn 13: Necta 2006 P^I Qn 3b and c

(b) A vessel containing 8.0g of oxygen at 25°C and a pressure of 5atm. Assume that the gas behaves ideally.

(i) What is the volume of the vessel?

(ii) What will be the final pressure when one mole of hydrogen molecules is added at 25°C without changing the volume.

(c) If the mixture is now exploded and allowed to cool to 25°C what will be the pressure of the gas in the vessel/ (Neglect the volume and vapour pressure of water).

Solution

Data

$$\text{Mass} = 8\text{g}$$

$$M_r = 32\text{gmol}^{-1}$$

$$T = (25 + 273)\text{K}$$

$$P = 5\text{atm}$$

B(i) Required: Volume of the vessel

Since the gas behaves ideally hence obeys ideal gas equation.

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

$$V = \frac{mRT}{P \cdot M_r}$$

$$V = \frac{8 \times 0.0821 \times 298}{5 \times 32}$$

$$V = 1.2233\text{L}$$

Hence volume of the vessel is 1.2233L.

(ii) Required: Final pressure when one mole of H_2 added.

ie. Find number of moles of O_2 present initially.

$$n = \frac{m}{M_r}$$

$$n = \frac{8\text{g}}{32\text{gmol}^{-1}}$$

$$n = 0.25 \text{ moles}$$

From

$$PV = nRT$$

$$P_i V = n_i RT$$

$$P_f = \frac{n_f RT}{V}$$

$$P_f = \frac{(0.25 + 1) \times 0.0821 \times 298}{1.2233}$$

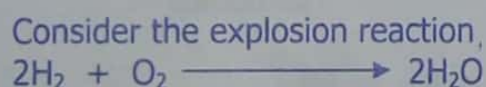
$$P_f = 25 \text{ atm.}$$

The final pressure would be 25 atm.

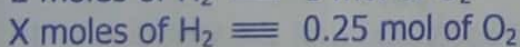
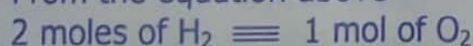
(c) Required: Pressure after explosion

Note:

Explosion result to formation of water. This result to decrease in the number of moles since some moles form water.



From the equation above



$$n_{\text{H}_2} = \frac{2 \times 0.25}{1}$$

$$n_{\text{H}_2} = 0.5 \text{ moles.}$$

- So after explosion the number of H_2 moles remain are $(1 - 0.5) = 0.5$ moles and no oxygen present. So the pressure would be due to this gas.

Then from,

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{0.5 \times 0.0821 \times 298}{1.2233} = 10 \text{ atm}$$

Hence pressure will be 10 atm.

Qn 14.

The equation for the metabolic breakdown of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is the same as

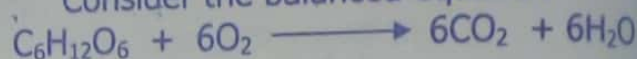
the equation for the combustion of glucose in air.



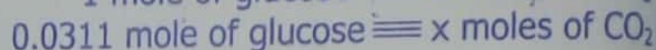
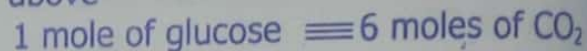
Calculate the volume of CO_2 produced at 37°C and 1atm when 5.6g of glucose is used up in the reaction.

Solution

Consider the balanced equation



From above



$$n_{\text{CO}_2} = \frac{0.0311 \times 6}{1}$$

$$n_{\text{CO}_2} = 0.19 \text{ moles}$$

Then from

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{0.19 \times 0.0821 \times 310}{1}$$

$$V = 4.836\text{L}$$

Then volume of CO_2 produced is 4.836L.

Qn 15: A gaseous compound is 78.14% Boron and 21.86% Hydrogen. At 27°C , 74.3ml of the gas exerted a pressure of 1.12atm. If the mass of the gas was 0.0934g, what is its molecular formula?

Solution

1st case:

From the data given in question above find the molar mass of the gas from ideal gas equation.

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{0.0934 \times 0.0821 \times 300}{1.12 \times 74.3 \times 10^{-3}}$$

$$M_r = 27.6 \text{ gmol}^{-1}$$

2nd case:

Find the empirical formula of a gaseous compound.
i.e.

	B	H
	78.14	21.86
	10.8	1
Divide by smallest	7.235	21.86
	7.235	7.235
	1	3

Then empirical formula of a gas is BH₃

3rd Case:

From molar mass and empirical formula find the molecular formula

Molecular formula is

$$(E.F)_n = M_r$$

$$(BH_3)_n = 27.6$$

$$10.8n + 3n = 27.6$$

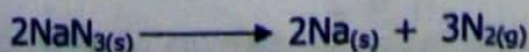
$$\frac{13.8n}{13.8} = \frac{27.6}{13.8}$$

$$n = 2$$

Then molecular formula is B₂H₆ (Diborane).

Qn. 16

Sodium azide (NaN₃) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN₃ as follows,

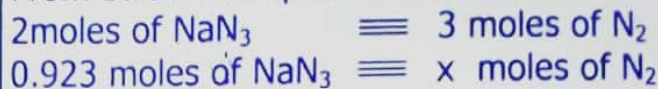


The nitrogen gas produced quickly inflates

the bag between the driver and the windshield and dashboard. Calculate the volume of N₂ generated at 80°C and 823mmHg by the decomposition of 60g of NaN₃.

Solution

From balanced equation above



$$n_{N_2} = \frac{0.923 \times 3}{2}$$

$$n_{N_2} = 1.385 \text{ mol}$$

We assume N₂ to behave ideal hence obeys the formula

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{1.385 \times 0.0821 \times 353 \times 760}{823}$$

$$V = 37L$$

Then volume of N₂ generated is 37L.

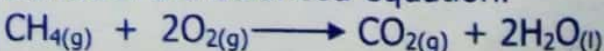
Qn 17:

A sample of methane gas having a volume of 2.8L at 25°C and 1.65atm was mixed with sample of Oxygen gas having a volume of 35.0L at 31°C and 1.25atm. The mixture was then ignited to form Carbondioxide and water. Calculate the volume of Carbondioxide formed at a pressure of 2.5atm and a temperature of 125°C.

Solution

1st case:

Consider the balanced equation.



2nd case:

Find the limiting reactant, which requires calculating the number of moles of each reactant. Number of moles of each is obtained from ideal gas equation.

$$\begin{aligned} PV &= nRT \\ n_{O_2} &= \frac{PV}{RT} \end{aligned}$$

$$n_{O_2} = \frac{1.65 \times 2.8}{0.0821 \times 298} = 0.189 \text{ mol}$$

Also

$$n_{O_2} = \frac{PV}{RT}$$

$$n_{O_2} = \frac{1.25 \times 35}{0.0821 \times 304}$$

$$n_{O_2} = 1.75 \text{ mol}$$

In the balanced equation for the combustion reaction 1 mol CH_4 required 2 mol O_2 . Thus the moles of O_2 required by 0.189 mol CH_4 can be calculated as follows

$$0.189 \text{ mol CH}_4 \times \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} = 0.378 \text{ mol O}_2$$

Since 1.75 mol O_2 is available, O_2 is in excess. The limiting reactant is CH_4 . The number of moles of CH_4 available will be used to calculate number of moles of CO_2 produced.

i.e.

From equation above



$$n_{CO_2} = \frac{0.189 \times 1}{1} = 0.189 \text{ mol}$$

From

$$PV_{CO_2} = nRT$$

$$V_{CO_2} = \frac{nRT}{P}$$

$$V_{CO_2} = \frac{0.189 \times 0.0821 \times 398}{2.5}$$

$$V_{CO_2} = 2.47 \text{ L}$$

Qn 18.

Chemical analysis of a gaseous compound showed that it contained 33% silicon and 67% fluorine by mass. At 35°C , 0.21 L of the compound exerted a pressure of 1.7 atm. If the mass of 0.21 L of the compound was 2.38 g, calculate the molecular formula of the compound.

Solution

1st Case:

Find the empirical formula of the compound.

i.e

Si	F
33	67
28	19
1.18	3.526
1.18	1.18
1	3

Divide by
Smallest

Then empirical formula of the gaseous compound is SiF_3 .

2nd Case:

From the data in the question, find the molar mass of the compound using ideal gas equation

From

$$PV = nRT$$

$$PV = \frac{mRT}{Mr}$$

$$Mr = \frac{mRT}{PV}$$

$$Mr = \frac{2.38 \times 0.0821 \times 308}{1.7 \times 0.21}$$

$$Mr = 168.6 \text{ gmol}^{-1}$$

3rd Case:

From the molar mass and empirical formula find the molecular formula.

Then

Molecular formula is

$$(EF)n = Mr$$

$$(\text{SiF}_3)n = 168.6$$

$$28n + 57n = 168.6$$

$$\frac{85n}{85} = \frac{168.6}{85}$$

$$n = 2$$

Then the molecular formula of gaseous compound Si_2F_6 .

Qn 19.

Dry ice is solid carbon dioxide. A 0.05g sample of dry ice is placed in an evacuated 4.6L vessel at 30°C. Calculate the pressure inside the vessel after all the dry ice has been converted to CO₂ gas.

Solution**Data:**

$$\begin{aligned} m &= 0.05\text{g} \\ V &= 4.6\text{L} \\ T &= (30 + 273)\text{K} \\ M_r &= 44\text{g mol}^{-1} \end{aligned}$$

From, $PV = nRT$

$$P = \frac{mRT}{M_r V}$$

$$P = \frac{0.05 \times 0.0821 \times 303}{44 \times 4.6}$$

$$P = 6.145 \times 10^{-3} \text{ atm}$$

Qn 20:

Calculate the density of hydrogen bromide (HBr) gas in grams per liter at 733mmHg and 46°C.

Solution**Data**

$$\begin{aligned} P &= 733 \text{ mmHg.} \\ T &= (46 + 273)\text{K} \\ M_r &= 81\text{g mol}^{-1} \end{aligned}$$

From

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

$$P = \frac{mRT}{VM_r}$$

$$\text{But } \frac{m}{V} = \rho$$

Then,

$$P = \frac{\rho RT}{M_r}$$

$$\rho = \frac{PM_r}{RT}$$

$$\rho = \frac{733 \times 81}{760 \times 0.0821 \times 319}$$

$$\rho = 2.98\text{g L}^{-1}$$

Qn 21

A compound has the empirical formula SF₄. At 20°C, 0.1g of the gaseous compound occupies a volume of 22.1mL and exert a pressure of 1.02 atm. What is the molecular formula of the gas?

Solution**Data**

$$\begin{aligned} T &= (20 + 273)\text{K} \\ m &= 0.1\text{g} \\ V &= 22.1\text{mL} \\ P &= 1.02 \text{ atm} \end{aligned}$$

1st Case:

From data above find the molar mass from $PV = nRT$

i.e.

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{0.1 \times 0.0821 \times 293}{1.02 \times 22.1 \times 10^{-3}}$$

$$M_r = 106.7\text{g mol}^{-1}$$

2nd Case:

Find the molecular formula from

$$(EF)_n = M_r$$

$$(\text{SF}_4)_n = 106.7$$

$$32n + 76n = 106.7$$

$$\frac{108n}{108} = \frac{106.7}{108}$$

$$n = 0.98 \approx 1$$

The molecular formula of the gas compound is SF₄.

Qn. 22

Methane, the principal component of natural gas, is used for heating and cooking. The combustion process is



If 15.0 moles of CH₄ are reacted, what is the volume of CO₂ in (litres) produced at 23.0°C and 0.985 atm?

Solution

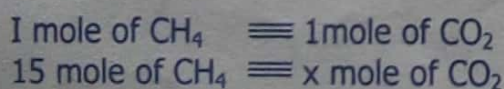
Data

$$n_{\text{CH}_4} = 15 \text{ moles}$$

$$T = (23 + 273)\text{K}$$

$$P = 0.985 \text{ atm}$$

From the balanced equation above, it appears that



$$n_{\text{CO}_2} = \frac{15 \times 1}{1} \approx 15 \text{ moles}$$

Then,

From

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{15 \times 0.0821 \times 296}{0.985}$$

$$V = 370 \text{ L.}$$

Qn. 23

A chemist has synthesized a greenish yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C

and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

Solution

Data

$$\rho = 7.71 \text{ g/L}$$

$$T = (36 + 273)\text{K}$$

$$P = 2.89984$$

From,

$$PV = nRT$$

$$PV = mRT$$

$$M_r = \frac{mRT}{VP}$$

$$M_r = \rho RT$$

$$M_r = \frac{7.71 \times 0.0821 \times 309}{2.89984}$$

$$M_r = 67.45 \text{ g mol}^{-1}$$

Then,

We can determine the molecular formula by trial and error method, using the knowledge of molar mass of chlorine and oxygen,

$$\begin{aligned} \text{Possible compounds of Cl and O are} \\ \text{ClO} &= M_r \text{ of } 51.45 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Cl}_2\text{O} = M_r \text{ of } 86.9 \text{ g mol}^{-1}$$

$$\text{ClO}_2 = M_r \text{ of } 67.45$$

Since the molar mass of 51.45 g mol⁻¹ for ClO is too low then not possible. Also the molar mass of 86.9 g mol⁻¹ for Cl₂O is too high then not possible. But the molar mass of ClO₂ almost matches then the answer is reasonable.

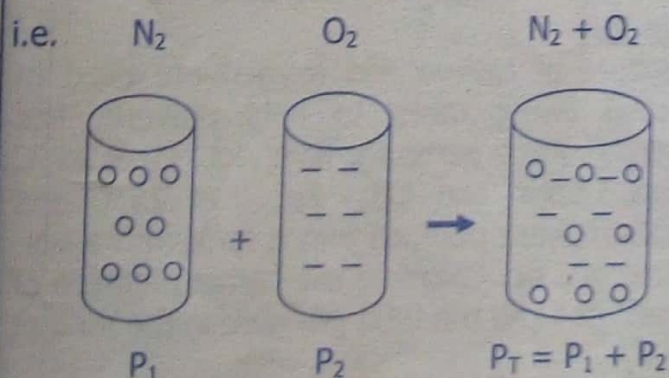
- Then the molecular formula of gaseous compound is ClO₂.

DALTON'S LAW OF PARTIAL PRESSURE.

- In 1801 John Dalton formulated the law concerned with the pressure in the mixture of gases. The law now known as Dalton's law of partial pressure and which states that

"In a mixture of gases which do not chemically react, the total pressure of the mixture is the sum of the partial pressures of the individual gases in the mixture at the same temperature".

- Partial pressure is the pressure of individual gas in the mixture of gases if it would occupy the whole space alone.
- Dalton's law can be explained by considering two gases say nitrogen and oxygen with pressure P_1 and P_2 respectively each contained in a 1L container. Then according to Dalton the total pressure in the mixture of nitrogen and oxygen is equal to the sum of pressure P_1 and P_2 .



MATHEMATICAL EXPRESSION OF PARTIAL PRESSURE.

To derive the partial pressure expression for ideal gases mixture consider P'_A and P'_B to be the pressure of gas A and B respectively with their corresponding number of moles, n_A and n_B contained in the vessel of volume V at a temperature T .

According to Dalton's law

$$P_T = P'_A + P'_B$$

Where,

P_T = Pressure total

From ideal gas equation

$$PV = nRT$$

For gas A.

$$P'_A V = n_A RT \quad \text{--- (i)}$$

For gas B.

$$P'_B V = n_B RT \quad \text{--- (ii)}$$

For total.

$$P_T V = n_T RT \quad \text{--- (iii)}$$

- By taking ratio of (i) and (iii)

$$\frac{P'_A V}{P_T V} = \frac{n_A RT}{n_T RT}$$

Or

$$\frac{P'_A}{P_T} = \frac{n_A}{n_T}$$

Then,

$$P'_A = \frac{n_A \times P_T}{n_T}$$

Similarly,

$$P'_B = \frac{n_B \times P_T}{n_T}$$

Where:

P'_A = Pressure of gas A in the mixture

P'_B = Pressure of gas B in the mixture

n_A = Number of moles of A

n_B = Number of moles of B

n_T = Total number of moles ($n_A + n_B$)

Note: The ratios $\frac{n_A}{n_T}$ and $\frac{n_B}{n_T}$ are called mole fractions.

Mole fraction: - Is the ratio of number of moles of a gas to the total number of moles in the mixture. It is denoted by χ (chi).

The sum of mole fractions of all the gases in the mixture must be unit.

i.e.

$$\frac{n_A}{n_T} + \frac{n_B}{n_T} = 1$$

Or

$$\chi_A + \chi_B = 1$$

APPLICATION OF DALTONS' LAW OF PARTIAL PRESSURE

One of the major application of the Dalton's law is to the gas collected over water (or any other moderate volatile liquid).

A gas collected over water contains water vapour also. Therefore, the total pressure exerted by this moist gas will be equal to the sum of the partial pressures of the dry gas and that of the water vapour.

i.e.

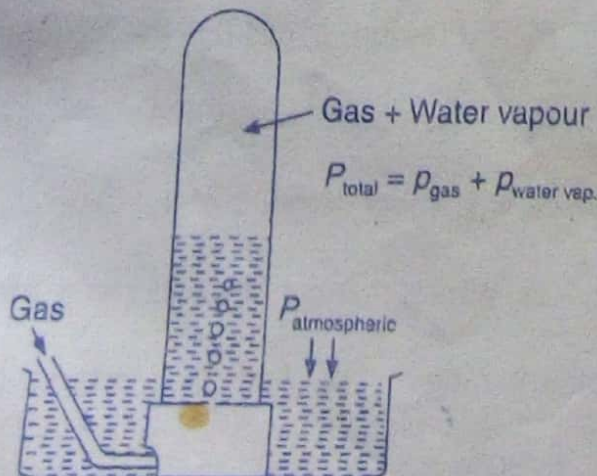
$$P_T = P'_{\text{gas}} + P'_{\text{water vapour.}}$$

Or

$$P'_{\text{gas}} = P_T - P'_{H_2O(g)}$$

Notice that the partial pressure of water vapour is called **aqueous tension**.

Diagram to show decomposition of $KClO_3$ in MnO_2 to produce O_2 which is collected over water.



Qn 24.

A neon-dioxygen mixture contains 70.6g dioxygen and 167.5g neon. If pressure of the mixture of gases in the cylinder is 25 atm. What is the partial pressure of dioxygen and neon in the mixture.

Solution

Data

$$n_{O_2} = \frac{70.6}{32} = 2.2 \text{ mol}$$

$$n_{Ne} = \frac{167.5}{20} = 8.375 \text{ mol.}$$

$$\chi_{O_2} = 0.21$$

$$\chi_{Ne} = 0.79$$

Then for O_2

$$P'_{O_2} = \chi_{O_2} \cdot P_T$$

$$P'_{O_2} = 0.21 \times 25 \text{ atm}$$

$$P'_{O_2} = 5.2 \text{ atm}$$

Also for Ne

$$P'_{Ne} = P_T - P'_{O_2}$$

$$P'_{Ne} = 19.75 \text{ atm.}$$

Qn 25.

Mixture of helium and oxygen are used in scuba diving tanks to help prevent "the bends". For a particular dive, 46L O_2 at 25°C and 1.0atm and 12L He at 25°C and 1.0atm were pumped into a tank with a volume of 5.0L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C .

Solution

1st Step:

Find number of moles of each gas using ideal gas law.

i.e.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

Then

$$n_{O_2} = \frac{1 \times 46}{0.0821 \times 298}$$

$$n_{O_2} = 1.9 \text{ mol.}$$

Also,

$$n_{\text{He}} = \frac{1 \times 12}{0.0821 \times 298}$$

$$n_{\text{He}} = 0.49 \text{ mol.}$$

2nd Case:

Since the tank containing the mixture of volume 5L then use $PV = nRT$ to get partial pressure.

i.e. For O_2

$$P = \frac{nRT}{V}$$

$$P = \frac{1.9 \times 0.0821 \times 298}{5}$$

$$P = 9.2 \text{ atm}$$

For He

$$P = \frac{nRT}{V}$$

$$P = \frac{0.49 \times 0.0821 \times 298}{5}$$

$$P = 2.4 \text{ atm.}$$

Also

$$P_T = P'_{\text{N}_2} + P'_{\text{O}_2}$$

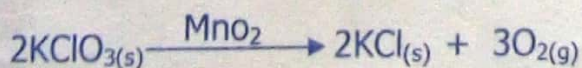
$$P_T = 9.2 + 2.4$$

$$P_T = 11.6 \text{ atm.}$$

Qn. 26

A sample of solid potassium chlorate was heated in small amount of MnO_2 in a test tube to yield gas according to the reaction equation.

i.e.



The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 650mL, and the vapour pressure of water at 22°C is 21tor. Calculate the partial pressure of O_2 in the gas collected and the mass of KClO_3 in the sample that was decomposed. (1torr = 1mmHg).

Solution

1st case:

Find the partial pressure of oxygen.

From Dalton's law

$$P_T = P'_{\text{O}_2} + P'_{\text{H}_2\text{O}(\text{vap})}$$

$$P'_{\text{O}_2} = 754 - 21 \text{ torr}$$

$$P'_{\text{O}_2} = 733 \text{ torr}$$

2nd case:

From ideal gas law find no. of moles of O_2

i.e.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{733 \times 650 \times 10^{-3}}{760 \times 0.0821 \times 298}$$

$$n = 2.59 \times 10^{-2} \text{ moles.}$$

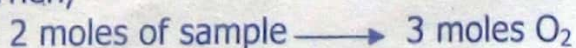
3rd Case:

From the balanced equation find no. of moles of KClO_3 used to get its mass.

Consider reaction



Then,



$$n_{\text{sample}} = \frac{2 \times 2.59 \times 10^{-2}}{3}$$

$$n_{\text{sample}} = 1.73 \times 10^{-2} \text{ moles}$$

Then number of moles of $\text{KClO}_3 = 1.73 \times 10^{-2}$ moles

But,

$$n = \frac{\text{mass}}{\text{Mr}}$$

$$= 1.73 \times 10^{-2} \times 122.5$$

$$= 2.12\text{g.}$$

Thus the original sample contained 2.12g.

Qn. 27

In a 3L bulb are introduced 0.2g of H_2 and 1.4g of N_2 at 200°C . Calculate,

- Mole fraction of each gas
- Total pressure of the mixture
- Partial pressure of each gas in the mixture.

Solution

Required: Mole fraction

Data

$$V_T = 3\text{L}$$

$$n_{\text{H}} = \frac{0.2\text{g}}{2\text{gmol}^{-1}} = 0.1 \text{ moles}$$

$$n_{\text{N}} = \frac{1.4\text{g}}{28\text{gmol}^{-1}} = 0.05 \text{ moles}$$

$$n_T = (0.1 + 0.05) \text{ moles}$$

Then

$$\text{Mole fraction, } \chi_{\text{H}} = \frac{n_{\text{H}_2}}{n_T}$$

$$= \frac{0.1}{0.15} = 0.67$$

$$\text{Mole fraction } \chi_{\text{N}} = \frac{0.05}{0.15} = 0.33$$

Hence the mole fraction of H_2 and N_2 are 0.67 and 0.33 respectively.

(b) required: Total pressure

From

$$P_T V_T = n_T R T$$

$$P_T = \frac{n_T R T}{V_T}$$

$$P_T = \frac{0.15 \times 0.0821 \times 473}{3}$$

$$P_T = 1.94 \text{ atm}$$

Then total pressure is 1.94 atm.

(c) Required: Partial pressure of each gas.

From

$$P'_{\text{H}_2} = \chi_{\text{H}_2} \cdot P_T$$

$$P'_{\text{H}_2} = 0.67 \times 1.94 \text{ atm}$$

$$P'_{\text{H}_2} = 1.3 \text{ atm.}$$

Partial pressure of H_2 is 1.3 atm.

Also

$$P'_{\text{N}_2} = P_T - P'_{\text{H}_2}$$

$$P'_{\text{N}_2} = 1.94 - 1.3$$

$$= 0.64 \text{ atm}$$

Partial pressure of N_2 is thus 0.64 atm.

Qn. 28

4dm^3 of oxygen at a pressure of 400Kpa and 1dm^3 of nitrogen at a pressure of 200Kpa are introduced into 2dm^3 vessel. What is the total pressure in the vessel?

Solution

Data . For O_2

$$V_1 = 4\text{dm}^3$$

$$P_1 = 400\text{Kpa}$$

$$V_2 = 2\text{dm}^3$$

$$P_2 = ?$$

From,

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{400 \times 4}{2}$$

$$P_2 = 800\text{Kpa.}$$

Then when oxygen contracts from 4dm^3 to 2dm^3 the pressure increases from 400Kpa to 800Kpa.

For N_2

$$V_1 = 1\text{dm}^3$$

Also,

$$n_{\text{He}} = \frac{1 \times 12}{0.0821 \times 298}$$

$$n_{\text{He}} = 0.49 \text{ mol.}$$

2nd Case:

Since the tank containing the mixture of volume 5L then use $PV = nRT$ to get partial pressure.

i.e. For O_2

$$P = \frac{nRT}{V}$$

$$P = \frac{1.9 \times 0.0821 \times 298}{5}$$

$$P = 9.2 \text{ atm}$$

For He

$$P = \frac{nRT}{V}$$

$$P = \frac{0.49 \times 0.0821 \times 298}{5}$$

$$P = 2.4 \text{ atm.}$$

Also

$$P_T = P'_{H_2} + P'_{O_2}$$

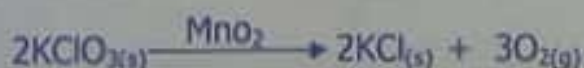
$$P_T = 9.2 + 2.4$$

$$P_T = 11.6 \text{ atm.}$$

Qn. 26

A sample of solid potassium chlorate was heated in small amount of MnO_2 in a test tube to yield gas according to the reaction equation.

i.e.



The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 650mL, and the vapour pressure of water at 22°C is 21tor. Calculate the partial pressure of O_2 in the gas collected and the mass of $KClO_3$ in the sample that was decomposed. (1torr = 1mmHg).

Solution

1st case:

Find the partial pressure of oxygen.

From Dalton's law

$$P_T = P'_{O_2} + P'_{H_2O(\text{vap})}$$

$$P'_{O_2} = 754 - 21 \text{ torr}$$

$$P'_{O_2} = 733 \text{ torr}$$

2nd case:

From ideal gas law find no. of moles of O_2

i.e.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{733 \times 650 \times 10^{-3}}{760 \times 0.0821 \times 298}$$

$$n = 2.59 \times 10^{-2} \text{ moles.}$$

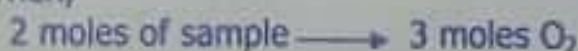
3rd Case:

From the balanced equation find no. of moles of $KClO_3$ used to get its mass.

Consider reaction



Then,



$$n_{\text{sample}} = \frac{2 \times 2.59 \times 10^{-2}}{3}$$

$$n_{\text{sample}} = 1.73 \times 10^{-2} \text{ moles}$$

Then number of moles of $KClO_3 = 1.73 \times 10^{-2}$ moles

But,

$$n = \frac{\text{mass}}{M_r}$$

$$\text{Mass} = n \times M_r$$

$$= 1.73 \times 10^{-2} \times 122.5$$

$$= 2.12\text{g.}$$

Thus the original sample contained 2.12g.

Qn. 27

In a 3L bulb are introduced 0.2g of H_2 and 1.4g of N_2 at 200°C . Calculate,

- Mole fraction of each gas
- Total pressure of the mixture
- Partial pressure of each gas in the mixture.

Solution

Required: Mole fraction

Data

$$V_T = 3\text{L}$$

$$n_{\text{H}} = \frac{0.2\text{g}}{2\text{gmol}^{-1}} = 0.1 \text{ moles}$$

$$n_{\text{N}} = \frac{1.4\text{g}}{28\text{gmol}^{-1}} = 0.05 \text{ moles}$$

$$n_T = (0.1 + 0.05) \text{ moles}$$

Then

$$\text{Mole fraction, } \chi_{\text{H}} = \frac{n_{\text{H}_2}}{n_T}$$

$$= \frac{0.1}{0.15} = 0.67$$

$$\text{Mole fraction } \chi_{\text{N}} = \frac{0.05}{0.15} = 0.33$$

Hence the mole fraction of H_2 and N_2 are 0.67 and 0.33 respectively.

(b) required: Total pressure

From

$$P_T V_T = n_T RT$$

$$P_T = \frac{n_T RT}{V_T}$$

$$P_T = \frac{0.15 \times 0.0821 \times 473}{3}$$

$$= 1.94 \text{ atm}$$

Then total pressure is 1.94 atm.

(c) Required: Partial pressure of each gas.

From

$$P'_{\text{H}_2} = \chi_{\text{H}_2} \cdot P_T$$

$$P'_{\text{H}_2} = 0.67 \times 1.94 \text{ atm}$$

$$P'_{\text{H}_2} = 1.3 \text{ atm.}$$

Partial pressure of H_2 is 1.3 atm.

Also

$$P'_{\text{N}_2} = P_T - P'_{\text{H}_2}$$

$$P'_{\text{N}_2} = 1.94 - 1.3$$

$$= 0.64 \text{ atm}$$

Partial pressure of N_2 is thus 0.64 atm.

Qn. 28

4dm^3 of oxygen at a pressure of 400Kpa and 1dm^3 of nitrogen at a pressure of 200Kpa are introduced into 2dm^3 vessel. What is the total pressure in the vessel?

Solution

Data . For O_2

$$V_1 = 4\text{dm}^3$$

$$P_1 = 400\text{Kpa}$$

$$V_2 = 2\text{dm}^3$$

$$P_2 = ?$$

From,

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{400 \times 4}{2}$$

$$P_2 = 800\text{Kpa.}$$

Then when oxygen contracts from 4dm^3 to 2dm^3 the pressure increases from 400Kpa to 800Kpa.

For N_2

$$V_1 = 1\text{dm}^3$$

$$\begin{aligned}P_1 &= 200\text{Kpa} \\V_1 &= 2\text{dm}^3 \\P_2 &= ?\end{aligned}$$

From,

$$\begin{aligned}P_1V_1 &= P_2V_2 \\P_2 &= \frac{P_1V_1}{V_2} \\P_2 &= \frac{200 \times 1}{2}\end{aligned}$$

$$P_2 = 100\text{Kpa}.$$

Then when nitrogen expands from 1dm^3 to 2dm^3 pressure decreases from 200Kpa to 100Kpa.

Then

$$P_T = P'_{O_2} + P'_{N_2}$$

$$P_T = 800\text{Kpa} + 100\text{Kpa}$$

$$P_T = 900\text{Kpa}.$$

Then total pressure is 900Kpa.

Qn 29.

Into a 10dm^3 vessel are introduced 4dm^3 of methane at a pressure of $2.02 \times 10^5\text{Nm}^{-2}$, 12.2dm^3 of ethane at a pressure of $3.5 \times 10^5\text{Nm}^{-2}$ and 1.5dm^3 of propane at a pressure of $1.01 \times 10^5\text{Nm}^{-2}$. What is the pressure of the resulting mixture.

Solution

1st Case:

Find partial pressure of each gas in the mixture.

For Methane:

$$\begin{aligned}V_1 &= 4\text{dm}^3 \\V_2 &= 10\text{dm}^3 \\P_1 &= 2.02 \times 10^5\text{Nm}^{-2} \\P_2 &= ?\end{aligned}$$

From,

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2}$$

$$P_2 = \frac{2.02 \times 10^5 \times 4}{10\text{dm}^3}$$

$$P_2 = 8.08 \times 10^4\text{Nm}^{-2}$$

The partial pressure of methane is $8.08 \times 10^4\text{Nm}^{-2}$

For ethane

$$\begin{aligned}P_1 &= 3.5 \times 10^5\text{Nm}^{-2} \\V_1 &= 12.5\text{dm}^3 \\V_2 &= 10\text{dm}^3 \\P_2 &= ?\end{aligned}$$

From,

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2}$$

$$P_2 = \frac{3.5 \times 10^5\text{Nm}^{-2} \times 12.5\text{dm}^3}{10\text{dm}^3}$$

$$P_2 = 4.375 \times 10^5\text{Nm}^{-2}.$$

Partial pressure of ethane is thus $4.375 \times 10^5\text{Nm}^{-2}$.

For propane

$$\begin{aligned}P_1 &= 1.01 \times 10^5\text{Nm}^{-2} \\V_1 &= 1.5\text{dm}^3 \\V_2 &= 10\text{dm}^3 \\P_2 &= ?\end{aligned}$$

FROM

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2}$$

$$P_2 = \frac{1.01 \times 10^5 \times 1.5}{10}$$

$$P_2 = 1.5 \times 10^4\text{Nm}^{-2}.$$

Then partial pressure of propane is $1.5 \times 10^4\text{Nm}^{-2}$.

2nd case:

Sum up the partial pressure to get the total pressure.

i.e.,

$$P_T = P'_{\text{meth}} + P'_{\text{eth}} + P'_{\text{prop}}$$

$$P_T = (8.08 \times 10^{-4} + 4.375 \times 10^{-3} + 1.5 \times 10^{-4}) \text{Nm}^{-2}$$

$$P_T = 5.3 \times 10^{-3} \text{Nm}^{-2}$$

Qn. 30

An enclosed bulb contain 0.01 moles of Helium gas and a sample of solid ammonium chloride (Neglect pressure of the solid) was measured at 27°C and found to be 114 mmHg. The sample was then heated at 327°C, all NH_4Cl decomposed to give gases according to the equation.

i.e



The final pressure after complete decomposition of NH_4Cl was 908 mmHg. Calculate.

(i) Partial pressure of HCl when the reactions completed

(ii) Amount of NH_4Cl present originally.

Solution

1st case:

Find the volume of the vessel

Data: For He

$$n = 0.01 \text{ moles}$$

$$T = 27 + 273 = 300\text{K}$$

$$P = 114 \text{mmHg}$$

From Ideal gas equation,

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{0.01 \times 0.0821 \times 300 \times 760}{114}$$

$$V = 1.642 \text{dm}^3$$

Then the volume of Helium is the same as volume of vessel which is 1.642dm³.

2nd Case:

Since volume of vessel is known, find the total number of moles at 327°C.

Given

$$V_T = 1.642 \text{dm}^3$$

$$P_T = 908 \text{mmHg}$$

$$T = 327 + 273 = 600\text{K}$$

From

$$P_T V_T = n_T R T$$

$$n_T = \frac{P_T V_T}{R T}$$

$$n_T = \frac{908 \times 1.642}{760 \times 0.0821 \times 600}$$

$$n_T = 0.04 \text{moles}$$

But NH_4Cl at 327°C decomposes to give equal number of moles of NH_3 and HCl .

i.e.



$$\text{Then } n_T = n_{\text{He}} + n_{\text{NH}_3} + n_{\text{HCl}}$$

$$0.04 = 0.01 + x + x$$

Then,

$$0.04 - 0.01 = 2x$$

$$\frac{0.03}{2} = \frac{2x}{2}$$

$$x = 0.015 \text{moles}$$

Then number of moles of HCl are 0.015 moles.

Then,

$$P'_{\text{HCl}} = \frac{n_{\text{HCl}}}{n_T} \times P_T$$

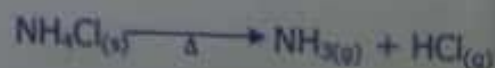
$$P'_{\text{HCl}} = \frac{0.015 \times 908}{0.04}$$

$$P'_{\text{HCl}} = 340.5 \text{mmHg}$$

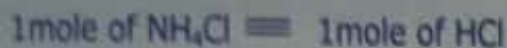
The partial pressure of HCl is 340.5mmHg.

(ii) Required: Amount of NH_4Cl present originally

Consider the reaction



From eqn above,



$$n_{\text{H}_2\text{O}} = 0.015 \text{ moles}$$

$$\text{But } n = \frac{\text{mass}}{\text{Molar mass}}$$

$$\begin{aligned} \text{mass} &= n \times M_r \\ &= 0.015 \times 53.5 \\ &= 0.8 \text{g.} \end{aligned}$$

Then amount of NH_4Cl present originally is 0.8g.

Qn. 31

A sample of magnesium carbonate (MgCO_3) is introduced in a 1 dm^3 flask. The flask is at start filled with air at 20°C and 1 atm. At 800°C all magnesium carbonate decomposed to give magnesium oxide and carbon dioxide. Final pressure was found to be 5 atm. Calculate,

- (i) The partial pressure of Carbon dioxide
- (ii) Amount of MgCO_3 present originally.

Solution

1st case:

Find number of moles of air in the container at 1 atm. Assume air to behave ideal.

i.e.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{1 \times 1}{0.0821 \times 293}$$

$$n = 0.0416 \text{ moles.}$$

Then number of moles of air is 0.0416 moles.

2nd case:

Find the total number of moles of air at 800°C

From,

$$P_T V_T = n_T RT$$

$$n_T = \frac{P_T V_T}{RT}$$

$$n_T = \frac{5 \times 1}{0.0821 \times 1073}$$

$$n_T = 0.0568 \text{ moles.}$$

Then

$$n_T = n_{\text{air}} + n_{\text{CO}_2}$$

$$n_{\text{CO}_2} = n_T - n_{\text{air}}$$

$$n_{\text{CO}_2} = 0.0568 - 0.0416 \text{ moles}$$

$$n_{\text{CO}_2} = 0.0152 \text{ moles.}$$

But,

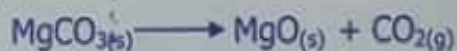
$$P'_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_T} \times P_T$$

$$P'_{\text{CO}_2} = \frac{0.0152 \times 5 \text{ atm}}{0.0568}$$

$$P'_{\text{CO}_2} = 1.34 \text{ atm}$$

(ii) Required: Amount of MgCO_3 originally

From,



$$n_{\text{MgCO}_3} = 0.015 \text{ moles}$$

$$\text{But, } n = \frac{m}{M_r}$$

$$m = n \times M_r$$

$$= 0.015 \times 84 \text{ moles.gmol}^{-1}$$

$$= 1.28 \text{g}$$

Then amount of MgCO_3 present originally was 1.28g.

Qn. 32

The mixture of gases C_2H_4 , C_2H_6 and Helium gas was heated in excess oxygen in a closed bulb at 300K and 680mmHg. All hydrocar-

bons composed to give carbon dioxide and water but Helium does not decompose. Carbon dioxide produced was collected in a separate beaker of 250cm^3 and found to exert a pressure of 561.3 mmHg . Helium also was collected in a separate beaker of 250cm^3 and found to have the pressure of 187.1 mmHg .

- Calculate the number of moles of helium present in the vessel.
- Calculate the number of moles of carbon dioxide produced
- Calculate the number of moles of hydrocarbons present originally.
- What is the volume of the original vessel?

Solution

(a) Required: Number of moles of helium

Data:

$$V = 250 \times 10^{-3}\text{dm}^3$$

$$P = 187.1\text{ mmHg}$$

$$T = 300\text{K}$$

$$n = ?$$

From,

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{187.1 \times 250 \times 10^{-3}}{760 \times 0.0821 \times 300}$$

$$n = 0.002 \text{ moles.}$$

(b) Required: Number of moles of CO_2 .

Data:

$$V = 250 \times 10^{-3}\text{dm}^3$$

$$P = 561.3\text{ mmHg}$$

$$T = 300\text{K}$$

$$n = ?$$

From,

$$PV = nRT$$

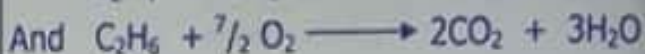
$$n = \frac{PV}{RT}$$

$$n = \frac{561 \times 250 \times 10^{-3}}{0.0821 \times 300 \times 760}$$

$$n = 0.0075 \text{ moles}$$

Required: Moles of hydrocarbons

Consider the reaction



Then from above,

$$2\text{moles of } \text{C}_x\text{H}_y \equiv 4\text{moles of } \text{CO}_2$$

$$x \text{ moles of } \text{C}_x\text{H}_y \equiv 0.0075 \text{ moles of } \text{CO}_2$$

$$n_{\text{C}_x\text{H}_y} = \frac{2 \times 0.0075}{4} = 0.00375 \text{ moles}$$

Hence number of moles of hydrocarbons are 0.00375 moles .

(d) Required: Volume of original vessel

Data:

$$P_T = 680\text{ mmHg}$$

$$T = 300\text{K}$$

$$n_T = (n_{\text{He}} + n_{\text{hydrocarbon}})$$

$$= (0.0025 + 0.00375)$$

$$V_T = ?$$

From,

$$PV = nRT$$

$$P_T V_T = n_T RT$$

$$V_T = \frac{n_T RT}{P_T}$$

$$V_T = \frac{0.00625 \times 0.0821 \times 300 \times 760}{680}$$

$$V_T = 0.172\text{dm}^3$$

Hence the volume of original vessel is 0.172dm^3 .

Qn. 33.

A mixture of gases at pressure of $1.01 \times 10^5 \text{ Nm}^{-2}$ has the volume composition of 30% CO , 50% O_2 and 20% CO_2 .

(a) What is the partial pressure of each gas?

(b) If the carbon dioxide is removed by addition of some pellets of sodium hydroxide, what will be the partial pressure of O_2 and CO ?

Solution

Required: Partial pressure of each gas.

According to Avogadro's law, the percentage by volume is equal to percentage by number of moles at the same condition of T and P.

Then,

$$\begin{aligned} P'_{CO} &= \frac{n_{CO}}{n_T} \times P_T \\ &= \frac{30}{100} \times 1.01 \times 10^5 \text{Nm}^{-2} \\ &= 3.03 \times 10^4 \text{Nm}^{-2}. \end{aligned}$$

Also

$$\begin{aligned} P'_{O_2} &= \frac{n_{O_2}}{n_T} \times P_T \\ &= \frac{50}{100} \times 1.01 \times 10^5 \text{Nm}^{-2} \\ &= 5.05 \times 10^4 \text{Nm}^{-2}. \end{aligned}$$

And

$$\begin{aligned} P'_{CO_2} &= \frac{n_{CO_2}}{n_T} \times P_T \\ &= \frac{20}{100} \times 1.01 \times 10^5 \text{Nm}^{-2} \\ &= 2.02 \times 10^4 \text{Nm}^{-2}. \end{aligned}$$

Then partial pressure of CO , O_2 and CO_2 are $3.03 \times 10^4 \text{Nm}^{-2}$, $5.05 \times 10^4 \text{Nm}^{-2}$ and $2.02 \times 10^4 \text{Nm}^{-2}$ respectively.

(b) If CO_2 is removed by the addition of pellets of sodium hydroxide, the partial pressure of O_2 and CO will remain the same as before. This is because partial pressure has no effect on the pressure of the other gases. The effect will be observed to the total pressure. Total pressure will decrease.

$$\text{i.e. } P_T = P'_{O_2} + P'_{CO}.$$

Qn 34.

50 cm^3 of carbon dioxide at 10^5Nm^{-2} are mixed 150 cm^3 of hydrogen at the same pressure. If the pressure of the mixture is $1.00 \times 10^5 \text{Nm}^{-2}$ what is the partial pressure of carbon dioxide?

Solution

Percentage by volume is equal to percentage by number of moles according to Avogadro's law.

Then,

$$\begin{aligned} V_T &= V_{CO_2} + V_{H_2} \\ &= 50 \text{ cm}^3 + 150 \text{ cm}^3 \\ &= 200 \text{ cm}^3 \end{aligned}$$

Then Mole fraction of CO_2 .

$$\frac{V_{CO_2}}{V_T} = \frac{50 \text{ cm}^3}{200} = 0.25$$

Also mole fraction of H_2

$$\frac{V_{H_2}}{V_T} = \frac{150}{200} = 0.75$$

Then

$$\begin{aligned} P'_{CO_2} &= \frac{n_{CO_2}}{n_T} \times P_T \\ &= \chi_{CO_2} \cdot P_T \\ &= 0.25 \times 1.00 \times 10^5 \text{Nm}^{-2} \end{aligned}$$

Then partial pressure of CO_2 is $2.525 \times 10^4 \text{Nm}^{-2}$.

Qn. 35

Oxygen is collected over water in a test tube at 33°C . The gas volume is measured to be 10 cm^3 . A manometer reads 85.5 kPa of air pressure. What volume would the dry oxygen occupy at s.t.p? Given that vapor pressure of water at 33°C is 5.0 KPa .

Solution

The gas collected is a mixture of oxygen and water vapour.

Thus,

$$P'_{O_2} = P_T - P_{\text{water}}$$

$$P'_{O_2} = 85.5 - 5.0 \text{ Kpa}$$

$$P'_{O_2} = 80.5 \text{ Kpa.}$$

Then the dry oxygen gas exert partial pressure of 80.5 Kpa at 33°C.

Use the general equation of a gas to reduce the volume of oxygen at S.T.P

Given,

$$P_1 = 80.5 \text{ Kpa} \quad P_2 = 101.3 \text{ Kpa}$$

$$V_1 = 10 \text{ cm}^3 \quad T_2 = 273 \text{ K}$$

$$T_1 = 306 \text{ K}$$

From,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{80.5 \times 10 \text{ cm}^3 \times 273}{306 \times 101.3}$$

$$V_2 = 7.1 \text{ cm}^3$$

Thus at s.t.p the dry oxygen would occupy about 7.1 cm³.

Qn. 36

Oxygen gas generated by decomposition of KClO3 is collected over water at 24°C. The volume of oxygen collected over water at 762 mmHg was found to be 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of water vapor at 24°C is 22.4 mmHg.

Solution

1st Case:

Find the partial pressure of oxygen

From,

$$P_T = P_{O_2} + P_{H_2O}$$

$$P'_{O_2} = P_T - P_{H_2O}$$

$$P'_{O_2} = 762 \text{ mmHg} - 22.4 \text{ mmHg}$$

$$P'_{O_2} = 740 \text{ mmHg.}$$

2nd Case:

Find the mass of oxygen from ideal gas equation.

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

$$m = \frac{PVM_r}{RT}$$

$$m = \frac{740 \times 0.128 \times 32}{760 \times 0.0821 \times 297}$$

$$m = 0.164 \text{ g.}$$

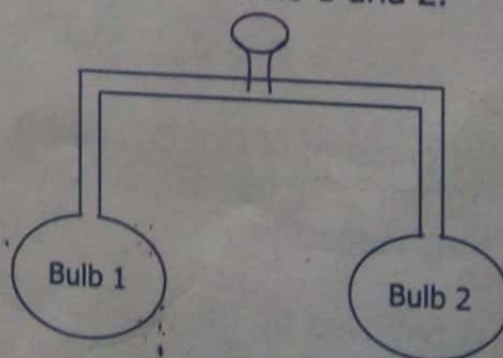
CONNECTED GAS CONTAINERS (Connected gas bulbs)

- suppose two gas containers of volume V_1 and V_2 are connected by a very thin capillary tube with negligible volume which has a tap at its centre at a temperature T .
- Effect of the gas in each bulb can be explained by considering two cases i.e. Before the tap is opened and after the tap is opened.

1. BEFORE THE TAP IS OPENED

- Before the tap is opened each gas in bulb 1 and 2 exerts its own pressure since some parameters apart from temperature are different in bulb 1 and 2.

i.e.



In Bulb 1

$$P = P_1$$

$$V = V_1$$

$$n = n_1$$

$$T = T$$

In Bulb 2

$$P = P_2$$

$$V = V_2$$

$$n = n_2$$

$$T = T$$

From ideal gas equation
 $PV = nRT$

(iii) Required: Partial pressure of each gas
Data

$$x_{O_2} = 0.33$$

$$x_{N_2} = 0.67$$

$$P_T = 4.6 \text{ atm}$$

For O_2

$$\begin{aligned} P'_{O_2} &= x_{O_2} \times P_T \\ &= 0.33 \times 4.6 \text{ atm} \\ &= 1.52 \text{ atm} \end{aligned}$$

For N_2

$$\begin{aligned} P_{N_2} &= x_{N_2} \times P_T \\ &= 0.67 \times 4.6 \text{ atm} \\ &= 3.08 \text{ atm} \end{aligned}$$

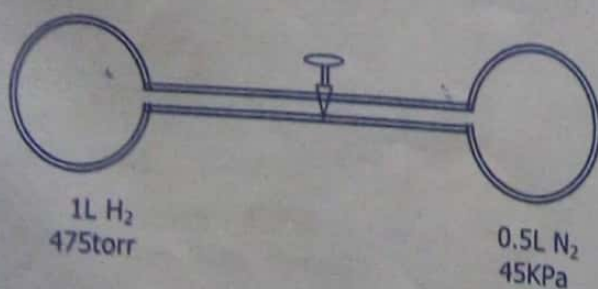
Then partial pressures of O_2 and N_2 are 1.52 atm and 3.08 atm respectively.

(iv) Required: Laws used in calculations

- Boyle's law
- Charles's law
- Dalton's law of partial pressure

Qn. 39

Consider the flask diagramed below. What is the total pressure in torr of H_2 and N_2 after the stopcock between the two flasks is opened?
i.e.



Solution

Data

For H_2

$$V_1 = 1L$$

$$P_1 = 475 \text{ torr}$$

For N_2

$$V_2 = 0.5L$$

$$P_2 = 337.53 \text{ torr}$$

From,

$$P_T = \frac{P_1 V_1 + P_2 V_2}{V_T}$$

$$P_T = \frac{(475 \times 1) + (337.53 \times 0.5)}{1.5}$$

$$P_T = 430 \text{ torr}$$

Then the total pressure is 430 torr.

Note:

- the formula $P_T V_T = P_1 V_1 + P_2 V_2$ is only applicable for connected bulbs of the same temperature.

- But if the temperature of one bulb (let say 2) changes from T_1 to T_2 then gas molecules in bulb₂ will gain kinetic energy and shift to bulb₁ until the final pressure P is attained.

- For example let x be number of moles of a gas shifted from bulb 2 to bulb 1. Then,

In bulb1

Pressure = P

Volume = V_1

Temperature T_1

Moles = $(n_1 + x)$

In bulb2

Pressure = P

Volume = V_2

Temperature = T_2

Moles $(n_2 - x)$

From ideal gas equation

$$PV = nRT$$

Becomes

$$PV_1 = (n_1 + x)RT_1 \text{ and } PV_2 = (n_2 - x)RT_2$$

OR

$$P = \frac{(n_1 + x)RT_1}{V_1} \text{ and } P = \frac{(n_2 - x)RT_2}{V_2}$$

Then obtain the number of moles in each bulb at the end after mixing compare (i) and (ii)

i.e.

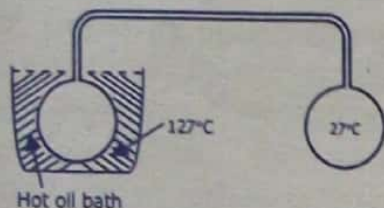
$$\frac{(n_1 + x)T_1}{V_1} = \frac{(n_2 - x)T_2}{V_2}$$

- If volume is the same for all bulbs but kept at different temperatures, then equation becomes,

$$(n_1 + x)T_1 = (n_2 - x)T_2$$

Qn. 40

Two flasks of equal volume were connected by a narrow tube of negligible volume, initially each flask was at 27°C and consists a total of 0.7 moles and 0.5 atm of hydrogen gas. Then one of the flask was immersed in a hot oil bath at 127°C while the other remained at 27°C as shown in the diagram below.



- Find the final pressure of H_2
- Calculate the number of moles of hydrogen gas in each flask at 127°C .

Solution

- Required: Final pressure

Data

$$T = 27 + 273\text{K} = 300\text{K}$$

$$P_T = 0.5\text{atm}$$

$$n_T = 0.7\text{moles.}$$

- From the data above find the total volume

From

$$PV = nRT$$

$$\text{Or } P_T V_T = n_T R_T$$

Then,

$$V_T = \frac{n_T R_T}{P_T}$$

$$V_T = \frac{0.7 \times 0.0821 \times 300}{0.5}$$

$$V_T = 34.482\text{dm}^3.$$

- Then volume of one flask = $\frac{34.482}{2}$
= 17.241dm^3

- Since they have equal volume, then they contain the same number of moles. i.e. 0.35 moles each.

Let x be number of moles shifted from bulb of 127°C temperature bulb to 27°C temperature bulb.

i.e.

27°C BULB	127°C BULB
$P = P$	$P = P$
$V = V_1 (17.241\text{dm}^3)$	$V = V_2 (17.241\text{dm}^3)$
$n = 0.35 + x$	$n = (0.35 - x)$
$T = T_1 = 300\text{K}$	$T = T_2 = 400\text{K}$

From,

$$PV = nRT$$

$$PV_1 = (n_1 + x)RT_1 \text{ and } PV_2 = (n_2 - x)RT_2$$

$$\text{But } V_1 = V_2$$

Then,

$$(n_1 + x)T_1 = (n_2 - x)T_2$$

Or

$$(0.35 + x)3 = (0.35 - x)4$$

$$1.05 + 3x = 1.4 - 4x$$

$$3x + 4x = 1.4 - 1.05$$

$$\frac{7x}{7} = \frac{0.35}{7}$$

$$x = 0.05$$

From

$$PV_1 = (n_1 + x)RT_1$$

$$P = \frac{(n_1 + x)RT_1}{V_1}$$

$$P = \frac{(0.35 + 0.05) \times 0.0821 \times 300}{17.241}$$

$$P = 0.57\text{atm.}$$

Hence the final pressure is 0.57atm.

- Required: Number of moles in each flask finally.

I.e

At 27°C

$$n = (n_1 + x)$$

$$n = (0.35 + 0.05)$$

$$n = 0.4\text{moles}$$

At 127°C

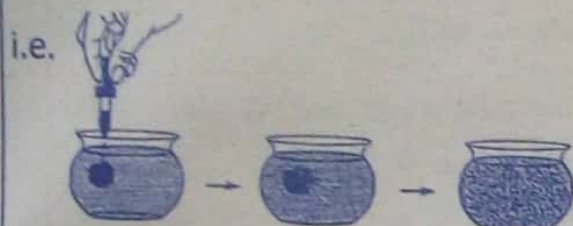
$$n = (n_2 - x)$$

$$n = (0.35 - 0.05)$$

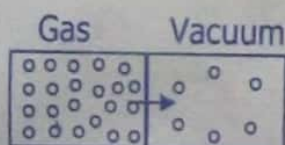
$$n = 0.3\text{ moles}$$

GRAHAM'S LAW OF GASEOUS DIFFUSION

- The diffusion is the process of gradually mixing of molecules of one gas with molecules of another gas due to their molecular motion, (Kinetic Energy).
- The diffusion always proceed from a region of high concentration to a region of lower concentration. The spread of a dye in water just due to the motion of their particle is an example of diffusion.



- Effusion process is quite different than the process of diffusion. The effusion is the process of forcing a gas through a pin hole (orifice) from one compartment to another empty (vacuum) compartment.



- In 1832 a Scottish Chemist Graham discovered that "under the same conditions of pressure and temperature the rate of diffusion/effusion of a gas is inversely proportional to the square root of its density". This is simply as Graham's law of diffusion/effusion.

Mathematically,

$$r \propto \frac{1}{\sqrt{\rho}}$$

Where

r = Rates of diffusion/effusion

ρ = Density of the gas.

Or

$$r = \frac{K}{\sqrt{\rho}}$$

- If there are two gases with densities P_1 and P_2 respectively under similar conditions of temperature and pressure, then the rates of diffusion or effusion can be written as,

$$r_1 = \frac{K}{\sqrt{\rho_1}} \quad r_2 = \frac{K}{\sqrt{\rho_2}}$$

- From these equations, one can write

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

- Recall ideal gas equation,

$$PV = nRT$$

But, $n = \frac{m}{Mr}$

$$PV = \frac{mRT}{Mr}$$

Or $P = \frac{mRT}{VMr}$

$$P = \frac{\rho RT}{Mr} \quad \text{Since } \frac{m}{V} = \rho$$

$$\rho = \frac{PMr}{RT}$$

$$\text{From, } r_1 = \frac{K}{\sqrt{\rho_1}} = \sqrt{\frac{K}{PMr_1/RT}}$$

And

$$r_2 = \frac{K}{\sqrt{\rho_2}} = \sqrt{\frac{K}{PMr_2/RT}}$$

If P and T are constants, then from

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

One can write,

$$\boxed{\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}}$$

- Thus from above equation it appears that the rate of diffusion/effusion of a gas is inversely proportional to the square root of its molar mass. This indicated that a gas with lower molecular mass will diffuse

faster.

- This equation is useful in qualitative way of understanding the relative rates of gases. For example, if you want to know, between H_2 and O_2 , which gas has the higher rate of diffusion?
- Just by knowing the molar masses of these gases, it is possible to get some idea about their relative rates. Since the rate is inversely proportional to the molar mass then H_2 with lower molar mass has greater rate of diffusion than O_2 .
- The rate of diffusion/effusion is measured in terms of the volume of the gas which gets diffused/effused in one second/or any other convenient unit of time.
- If t_1 and t_2 are the times taken for the diffusion/effusion of volumes V_1 and V_2 respectively of a gas 1 and 2 then,

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

- If equal volumes are made to diffuse out i.e.

$$\frac{V_1}{t_1} \div \frac{V_2}{t_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

Or

$$\boxed{\frac{t_2}{t_1} = \sqrt{\frac{Mr_2}{Mr_1}}}$$

- Now if the two gases diffuse at the same time, then,

$$\frac{V_1}{t} \div \frac{V_2}{t} = \sqrt{\frac{Mr_2}{Mr_1}}$$

Or

$$\boxed{\frac{V_1}{V_2} = \sqrt{\frac{Mr_2}{Mr_1}}}$$

EXAMPLE OF PROBLEMS ON GRAHAM'S LAW

Qn. 41

A sample of N_2O effuses from a container in 42 seconds. How long would it take the same amount of gaseous I_2 to effuse from the

same container under identical conditions?

Solution

Data

$$Mr_{N_2O} = 44 \text{ g mol}^{-1} (Mr_1)$$

$$Mr_{I_2} = 254 \text{ g mol}^{-1} (Mr_2)$$

$$t_{N_2O} = 42 \text{ sec. } (t_1)$$

From,

$$\frac{t_2}{t_1} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{t_2}{42} = \sqrt{\frac{254}{44}}$$

N_2O

$$t_2 = \sqrt{\frac{254}{44}} \times 42$$

$$t_2 = 101 \text{ seconds.}$$

Qn. 42

What is the molecular weight of a gas which diffuses $1/50$ as fast as hydrogen?

Solution

Let the rate of diffusion of hydrogen be x so that of unknown gas be $1/50x$.

Then,

$$\frac{r_{H_2}}{r_u} = \sqrt{\frac{Mr_u}{Mr_{H_2}}}$$

$$\frac{x}{1/50x} = \sqrt{\frac{Mr_u}{2}}$$

$$\frac{x}{0.02x} = \sqrt{\frac{Mr_u}{2}}$$

$$\frac{1}{0.02} = \sqrt{\frac{Mr_u}{2}}$$

$$\left(\frac{1}{0.02}\right)^2 = \frac{Mr_u}{2}$$

$$Mr_u = (1/0.02)^2 \times 2$$

$$Mr_u = 5000 \text{ g mol}^{-1}$$

Qn. 43

If equal amounts of helium and Argon are placed in a porous container and allowed to escape, which gas will escape faster and how much faster?

Solution

Since the Molar mass of He = 4g mol^{-1} and that of argon is 39.95g mol^{-1} then a gas with low molecular mass will escape faster according to Graham's law. How faster consider.

$$r_1 = r_{\text{Helium}}$$

and

$$r_2 = r_{\text{argon}}$$

Hence,

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{39.95}{4}}$$

$$\frac{r_1}{r_2} = 3.16$$

$$r_1 = 3.16r_2$$

Then helium will diffuse 3.16 as fast as Argon.

Qn. 44

If a molecule of CH_4 diffuses a distance of 0.53m from a point source, calculate the distance (in meters) that a molecule of N_2 would diffuse under the same condition for the same period of time.

Let velocity of CH_4 be C_1 and that of N_2 be C_2 .

Given,

$$Mr_1 = 16\text{g mol}^{-1}$$

$$Mr_2 = 28\text{g mol}^{-1}$$

From,

$$\text{Distance of } \text{CH}_4 = 0.53\text{m}$$

$$\text{Distance of } \text{N}_2 = x$$

From,

$$\frac{C_1}{C_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{C_1}{C_2} = \sqrt{\frac{28}{16}}$$

$$\frac{C_1}{C_2} = 1.323$$

$$C_1 = 1.323C_2 \dots\dots\dots (i)$$

But,

$$\text{Velocity} = \frac{\text{distance}}{\text{Time}}$$

$$C_1 = \frac{0.53\text{m}}{t}$$

And,

$$C_2 = \frac{x}{t}$$

Then from eqn. (i) above

$$\frac{0.53}{t} = \frac{1.323x}{t}$$

Or

$$\frac{0.53}{1.323} = \frac{1.323x}{1.323}$$

$$x = 0.4\text{m.}$$

Then distance in which N_2 would diffuse is 0.4m.

Qn. 45

A 3L sample of helium was placed in a container fitted with a porous membrane. Half of the helium effuses through the membrane in 25hrs. A 3L sample of oxygen was placed in an identical container. How many hours will it take for half of the oxygen to effuse through the membrane.

Solution

1st Case: Determine helium's rate of effusion

From,

$$\text{Rate}_1 = \frac{V}{t_1} = \frac{1.5\text{L}}{25\text{hr}} = 0.06\text{Lhr}^{-1}$$

From

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{0.06}{r_2} = \frac{32}{4}$$

$$r_2 = 0.06 \div \sqrt{\frac{32}{4}}$$

Then $r_2 = 0.0212 \text{Lhr}^{-1}$.

Then rate of oxygen in liters per hour is thus 0.0212Lhr^{-1} .

- In 1.5L it is

$$\begin{array}{lcl} \text{If } 0.0212 & \longrightarrow & 1\text{hr} \\ 1.5\text{L} & \longrightarrow & ? \text{ hr} \end{array}$$

$$\text{hr} = \frac{1.5\text{L}}{0.0212 \text{L.h}^{-1}}$$

$$= 70.7\text{hrs.}$$

Qn. 46

0.5m^3 of carbon dioxide diffused through a porous pot, in 10 seconds. What volume of sulphur dioxide will diffuse through it in 10 seconds under the same conditions of temperature and pressure?

Solution

- Since time taken for diffusions the same, then

$$\frac{V_1}{V_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

Given,

$$V_{\text{CO}_2} = 0.5\text{m}^3 (V_1)$$

$$V_{\text{SO}_2} = ? (V_2)$$

$$Mr_{\text{CO}_2} = 44 \text{gmol}^{-1} (Mr_1)$$

$$Mr_{\text{SO}_2} = 64\text{gmol}^{-1} (Mr_2)$$

From,

$$\frac{V_{\text{CO}_2}}{V_{\text{SO}_2}} = \sqrt{\frac{Mr_{\text{SO}_2}}{Mr_{\text{CO}_2}}}$$

$$\frac{0.5\text{m}^3}{V_{\text{SO}_2}} = \sqrt{\frac{64}{44}}$$

$$V_{\text{SO}_2} = 0.41\text{m}^3$$

Then volume of SO_2 that will diffuse is 0.41m^3 .

Qn. 47

In an experiment 100cm^3 of H_2 takes 5 seconds and unknown gas takes 20 seconds to diffuse through a porous membrane. Determine the density of the unknown gas relative to that of hydrogen gas.

Solution

Let variables of hydrogen be 1 and those for unknown gas be 2.

Data

$$V_1 = 100\text{cm}^3$$

$$t_1 = 5\text{seconds}$$

$$V_2 = 100\text{cm}^3$$

$$t_2 = 20\text{seconds}$$

$$r_1 = 20\text{cm}^3\text{sec}^{-1}$$

$$r_2 = 5\text{cm}^3\text{sec}^{-1}$$

From Graham's law,

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Substitute the known values.

$$\frac{20}{5} = \sqrt{\frac{\rho_2}{\rho_1}}$$

$$4 = \sqrt{\frac{\rho_2}{\rho_1}}$$

$$4^2 = \frac{\rho_2}{\rho_1}$$

$$\rho_2 = 16\rho_1$$

Then the density of unknown gas is 16times that of hydrogen gas.

Qn. 48

The hydrocarbon with the general formula of C_nH_{2n+2} is found to diffuse twice as the rate of SO_2 at the same condition of temperature. Determine the molecular formula of the hydrocarbon. Name the hydrocarbon if possible.

Solution

Let the rate of diffusion of hydrocarbon be $2a$ and that of SO_2 be a . But hydrocarbon diffuses twice as much as the rate of SO_2 .

Then,

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{2a}{a} = \sqrt{\frac{64}{Mr_1}}$$

$$2 = \sqrt{\frac{64}{Mr_1}}$$

$$2^2 = \frac{64}{Mr_1}$$

$$Mr_1 = \frac{64}{4} = 16 \text{ g mol}^{-1}$$

From,

$$C_nH_{2n+2} = 16$$

$$12n + 2n + 2 = 16$$

$$14n = 16 - 2$$

$$\frac{14n}{14} = \frac{14}{14}$$

$$n = 1$$

Therefore the molecular formula of the hydrocarbon is CH_4 . This hydrocarbon is methane.

Qn. 49

In running a diffusion experiment, ammonia is found to diffuse 30 cm^3 during the time hydrogen chloride diffuses 20 cm^3 . Calculate the percentage deviation from Graham's law.

Solution

The experimentally determined ratio is of NH_3 over r_2 of HCl

i.e.

$$\frac{V_1}{V_2} = \frac{30}{20} = 1.5$$

- Find the ratio predicted from Graham's law.

i.e.

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{36.5}{17}}$$

$$\frac{r_1}{r_2} = 1.465$$

$$r_1 = 1.465r_2$$

Ammonia diffuses 1.465 times faster than hydrogen chloride.

- Find the percentage deviation
i.e.

$$\frac{1.5 - 1.465}{1.5} = 2.33\%$$

Then percentage deviation from Graham's law is 2.33%.

Qn. 50

Why are the rates of diffusion of N_2 gas and CO gas almost identical at the same temperature?

Solution

(i) The speed of a gas is given by

$$U_{r.m.s} = \sqrt{\frac{3RT}{Mr}}$$

Where,

Mr = is the molar mass of the gas in kg mol^{-1} .

(ii) The molecular weights are
 $N_2 = 0.028014 \text{ Kg/mol}$
 $CO = 0.028010 \text{ Kg/mol}$

- Without solving the formula for speeds you should be able to see that the speed will be nearly identical. The values (R and T) are going to be the same.
- The diffusion rates for N_2 gas and CO gas are very nearly the same at the same temperature because the two substances have very nearly the same molecular weights.

Qn. 51

200 cm^3 of oxygen take 250 seconds to diffuse through a porous diaphragm. Under identical conditions, 200 cm^3 of unknown gas x take 177 seconds to diffuse. What is the relative molecular mass of the unknown substance gas?

Solution

Let t_1 be the time of oxygen to diffuse and t_2 time taken for unknown gas to diffuse, then,

$$\begin{aligned} t_1 &= 250 \text{ sec} \\ t_2 &= 177 \text{ sec} \\ V_1 &= 200 \text{ cm}^3 \\ V_2 &= 200 \text{ cm}^3 \\ Mr_1 &= 32 \text{ g/mol}^{-1} \end{aligned}$$

From,

$$r_1 = \frac{V_1}{t_1} = \frac{200 \text{ cm}^3}{250 \text{ sec}} = 0.8 \text{ cm}^3 \text{ sec}^{-1}$$

$$r_2 = \frac{V_2}{t_2} = \frac{200 \text{ cm}^3}{177 \text{ sec}} = 1.13 \text{ cm}^3 \text{ sec}^{-1}$$

From,

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{0.8}{1.13} = \sqrt{\frac{Mr_2}{32}}$$

$$\left(\frac{0.8}{1.13}\right)^2 = \frac{Mr_2}{32}$$

$$Mr_2 = \left(\frac{0.8}{1.13}\right)^2 \times 32$$

$$Mr_2 = 16 \text{ g/mol}^{-1}$$

Then relative molecular mass of unknown gas is 16.

Qn. 52

A gaseous compound x contains 46.1% C and 53.9N. In 20 seconds, 50 cm^3 of x diffuse in a porous plug and the same volume of oxygen diffused in 15.7 seconds.

- Calculate the molecular formula of compound x.
- What volume of carbon dioxide will diffuse in 20 seconds under the same condition?

Solution

Let variables of gaseous compound x be 1 and that of oxygen be 2.

Data

$$\begin{aligned} t_1 &= 20 \text{ sec} \\ t_2 &= 15.7 \text{ sec} \\ Mr_1 &= ? \\ Mr_2 &= 32 \text{ g/mol}^{-1} \end{aligned}$$

1st Case:

Find the molar mass of gaseous compound x,

From,

$$\frac{t_2}{t_1} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{15.7}{20} = \sqrt{\frac{32}{Mr_1}}$$

$$\left(\frac{15.7}{20}\right)^2 = \frac{32}{Mr_1}$$

$$Mr_1 = 32 \div \left(\frac{15.7}{20}\right)^2$$

$$Mr_1 = 52 \text{ g/mol}^{-1}$$

2nd case:

Find the empirical formula of the compound.

i.e.

C	N
<u>46.1</u>	<u>53.9</u>
12	14

Divide by the smallest

<u>3.84</u>	<u>3.85</u>
3.84	3.84
1	1

Then empirical formula of compound x = CN

3rd case:

Find the molecular formula

i.e.

$$\begin{aligned} Mr &= (EF)n \\ 52 &= (CN)n \\ 52 &= 12n + 14n \\ \underline{52} &= \underline{26n} \\ 26 & \quad 26 \end{aligned}$$

$$n = 2$$

Then molecular formula is C_2N_2 .

(ii) Required: Volume of CO_2 diffused

Solution

Let variables of oxygen be 1 and CO_2 be 2.

i.e.

Data

$$r_1 = \frac{50}{15.7} = 3.185 \text{ (rate of } O_2)$$

$$r_2 = \frac{v_2}{20} \text{ (rate } CO_2)$$

From,

$$\frac{r_1}{r_2} = \frac{3.185 \times 20}{2} = \frac{Mr_2}{Mr_1}$$

$$\frac{63.7}{V_2} = \frac{44}{32}$$

$$\frac{63.7}{V_2} = 1.173$$

$$V_2 = \frac{63.7}{1.173}$$

$$V_2 = 54.3 \text{ cm}^3$$

Then volume of CO_2 that will diffuse is 54.3 cm^3 .

Qn. 53

On analysis a compound gave 90.35% x and 9.65% H and found to diffuse through a porous plug of $2/3$ of velocity of nitrogen. Deduce the molecular formula of the compound ($x = 28.1 \text{ g mol}^{-1}$, $H = 1 \text{ g mol}^{-1}$ and $N = 14 \text{ g mol}^{-1}$).

Solution

Let velocity of nitrogen be "a" so that of the compound be $2/3 a$.

Data

$$\text{Velocity of compound } C_1 = 2/3 a.$$

$$\text{Velocity of Nitrogen } C_2 = a$$

$$\text{Molar mass of } N_2 = 28 \text{ g mol}^{-1}$$

$$\text{Mr of Cpd} = ?$$

From,

$$\frac{C_1}{C_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{0.667a}{a} = \sqrt{\frac{Mr_2}{28}}$$

$$0.667 = \sqrt{\frac{28}{Mr_2}}$$

$$(0.667)^2 = \frac{28}{Mr_2}$$

$$Mr_2 = 28 \div (0.667)^2$$

$$Mr_2 = 63 \text{ g mol}^{-1}.$$

Find the empirical formula

X	H
<u>90.35</u>	<u>9.65</u>
28.1	1

Divide by Smallest

<u>3.22</u>	<u>9.65</u>
3.22	3.22
1	3

Then empirical formula of the compound is XH_3

From,

$\text{Mr} = (\text{EF})_n$ we get molecular formula

$$63 = (\text{XH}_3)_n$$

$$63 = 28.1n + 3n$$

$$\frac{63}{31.1} = \frac{31.1n}{31.1}$$

$$n = 2$$

The molecular formula is thus X_2H_6 .

Qn. 54

A sample of tear gas is released in the last row seats in a lecture hall. At the same time a sample of a laughing gas is released in the first row seats. After a time the last 10 rows of students are crying and the first 20 rows of students are laughing. If the laughing gas is N_2O what is the molar mass of the tear gas?

Solution

Data

Rate of diffusion of tear gas = 10 units.

Rate of diffusion of laughing gas = 20 units.

Molar mass of laughing gas = 44g mol^{-1} .

Mr of tear gas = ?

From,

$$\frac{\text{Rate of diffusion of tear gas}}{\text{Rate of diffusion of laughing gas}} = \sqrt{\frac{\text{Mr of laughing}}{\text{Mr of tear}}}$$

$$\frac{10}{20} = \sqrt{\frac{44}{\text{Mr tear}}}$$

$$\left(\frac{10}{20}\right)^2 = \frac{44}{\text{Mr tear}}$$

$$\text{Mr tear} = \frac{44}{0.25}$$

$$\text{Mr tear gas} = 176\text{g mol}^{-1}.$$

Qn. 55

Hydrogen diffused 7.94 times faster as the same volume of gaseous fluoride of phosphorus (under the same condition). Calculate the molar mass of the fluoride of phosphorus.

Solution

Let the rate of diffusion of gaseous fluoride of phosphorus be x so that of hydrogen be $7.94x$.

Then from

$$\frac{r_{\text{H}_2}}{r_2} = \frac{\text{Mr}_2}{\text{Mr}_1}$$

$$\frac{7.94x}{x} = \frac{\text{Mr}_2}{2}$$

$$\text{Mr}_2 = 2 \times (7.94)^2$$

$$\text{Mr}_2 = 126\text{g mol}^{-1}.$$

Then the molar mass of gaseous fluoride of phosphorus is 126g mol^{-1} .

Now consider

PF_n to be the empirical formula.

Then

$$\text{PF}_n = 126$$

$$31 + 19n = 126$$

$$19n = 126 - 31$$

$$\frac{19n}{19} = \frac{95}{19}$$

$$n = 5$$

Then from PF_n formula of fluoride of phosphorus is PF_5 .

Qn 56.

At 127°C the helium gas moves with the velocity of 12m s^{-1} at the same temperature a diatomic gas Y moves with velocity of 8m/s . What is the molar mass of gas Y?

Solution

Data

$$r_{\text{He}} = r_1 = 12\text{m/s}$$

$$r_Y = r_2 = 8\text{m/s}$$

$$\text{Mr}_1 = 4\text{g mol}^{-1}$$

$$\text{Mr}_2 = ?$$

From,

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{12}{8} = \sqrt{\frac{Mr_2}{4}}$$

$$\left(\frac{12}{8}\right)^2 = \frac{Mr_2}{4}$$

$$Mr_2 = \left(\frac{12}{8}\right)^2 \times 4$$

$$Mr_2 = 9 \text{ gmol}^{-1} \text{ (monatomic)}$$

Since it is diatomic i.e. (Y_2) then its molar mass would be $9 \times 2 = 18 \text{ gmol}^{-1}$.

Qn. 57

At 27°C hydrogen leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minutes. After the effusion of gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 moles. If the volume of the container is 3 litres, what is the molecular weight of unknown gas?

Solution

From ideal gas equation

$$PV = nRT$$

Or

$$P_T V_T = n_T R_T$$

$$n_T = \frac{P_T V_T}{R_T}$$

$$n_T = \frac{6 \times 3}{0.0821 \times 300}$$

$$n_T = 0.73 \text{ moles.}$$

But,

$$n_T = n_H + n_{\text{gas}}$$

$$0.73 = 0.7 + n_{\text{gas}}$$

$$n_{\text{gas}} = 0.73 - 0.7$$

$$n_{\text{gas}} = 0.03 \text{ moles.}$$

From Graham's law.

$$\frac{n_{H_2}}{n_{\text{gas}}} = \sqrt{\frac{Mr_{\text{gas}}}{Mr_{H_2}}}$$

$$\frac{0.7}{0.03} = \sqrt{\frac{Mr_{\text{gas}}}{2}}$$

$$\left(\frac{0.7}{0.03}\right)^2 = \frac{Mr_{\text{gas}}}{2}$$

$$Mr_{\text{gas}} = 1088 \text{ gmol}^{-1}$$

Hence molecular weight of unknown gas 1088.9 gmol^{-1} .

Qn. 58

The mixture of CO and CO_2 diffuses through a porous diaphragm in one half of the time taken for the same volume of bromine vapor. What is the composition by volume of the mixture gases?

Solution

Let t be the time taken for diffusion of bromine vapor so that one half t ($0.5t$) be the time for the mixture.

From,

$$\frac{t_2}{t_1} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{t_{\text{mix}}}{t_{\text{Br}}} = \sqrt{\frac{Mr_{\text{mix}}}{Mr_{\text{Br}_2}}}$$

$$\frac{0.5t}{t} = \sqrt{\frac{Mr_{\text{mix}}}{160}}$$

$$0.5^2 = \frac{Mr_{\text{mix}}}{160}$$

$$Mr_{\text{mix}} = 160 \times (0.5)^2$$

$$Mr_{\text{mix}} = 40 \text{ gmol}^{-1}$$

This 40 gmol^{-1} is the apparent molar mass which is obtained as,

$$\text{App. Mr} = \text{Actual Mr} \times \text{Mole fraction}$$

- Let x be mole fraction of CO and y be mole fraction of CO_2 .

i.e.

$$\begin{cases} 40 = 28x + 44y \\ 1 = x + y \end{cases}$$

Solving for x and y simultaneously we get,

$$x = 0.25 \text{ or } 25\%$$

$$y = 0.75 \text{ or } 75\%$$

Then percentage by volume of the mixture gases are 25% CO and 75% CO_2 .

Qn. 59

The time taken for effusion of equal volume of CO_2 and a mixture of CO_2 and CO are 32 seconds and 27 seconds respectively. Calculate the apparent molar mass of the mixture gases and composition of each gas in the mixture.

Solution

Data

$$M_{r1} = 44 \text{ g mol}^{-1} (\text{CO}_2)$$

$$M_{r2} = (\text{CO}_2, \text{CO})$$

$$t_1 = 32 \text{ second}$$

$$t_2 = 27 \text{ seconds}$$

From

$$\frac{t_2}{t_1} = \sqrt{\frac{M_{r2}}{M_{r1}}}$$

$$\frac{27}{32} = \sqrt{\frac{M_{r2}}{44}}$$

$$\left(\frac{27}{32}\right)^2 = \frac{M_{r2}}{44}$$

$$M_{r2} = 0.7119 \times 44$$

$$M_{r2} = 31.32 \text{ g mol}^{-1}$$

Then apparent molar mass of the mixture gases is 31.32 g mol^{-1} .

Then,

$$\text{App. Mr} = \text{Actual Mr} \times \text{Mole fraction}$$

Let x be mole fraction of CO_2 and y mole fraction of CO, then

$$\begin{cases} 31.32 = 44x + 28y \\ 1 = x + y \end{cases}$$

- Solve the two equation simultaneously.

Then,

$$x = 0.21 \text{ or } 21\%$$

$$y = 0.79 \text{ or } 79\%$$

Then the compositions of CO_2 and CO in the mixture are 21% and 79% respectively.

Qn 60.

The composition of the equilibrium mixture ($\text{Cl}_2 \rightleftharpoons 2\text{Cl}$), which is attained at 1200°C is determined by measuring the rate of effusion through a pin hole. It is observed that at 180 mmHg pressure, the mixture effuses 1.16 times as faster as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociate into atoms (Atomic wt of Kr = 84)

Solution

From Graham's law,

$$\frac{\text{Rate of Cl}_2 - \text{Cl mixture}}{\text{Rate of Krypton}} = \sqrt{\frac{M_{r \text{ of Kr}}}{\text{App. Mr}}}$$

$$1.16 = \frac{84}{\text{App Mr}}$$

$$1.16^2 = \frac{84}{\text{App. Mr}}$$

$$\text{App. Mr} = 84 \div 1.16^2$$

$$\text{App. Mr} = 62.4 \text{ g mol}^{-1}$$

- Now if α is the fraction of Cl_2 molecules dissociated into atoms, then,



Total number of atoms and molecules.

$$1 - \alpha + 2\alpha = 1 + \alpha$$

Then,

Mole fractions

$$x_{\text{Cl}_2} = \frac{(1 - \alpha)}{(1 + \alpha)}$$

$$\text{and } \chi_{\text{Cl}} = \frac{2\alpha}{1 + \alpha}$$

Therefore,

Apparent $M_r = \text{Atual } M_r \times \text{Mole fraction}$

i.e.

$$M_{r_{\text{Cl}_2}} \times \frac{(1-\alpha)}{(1+\alpha)} + M_{r_{\text{Cl}}} \times \frac{2\alpha}{(1+\alpha)} = 62.4$$

$$71 \times \frac{(1-\alpha)}{(1+\alpha)} + \frac{71\alpha}{1 + \alpha} = 62.4$$

This gives

$$\frac{71 - 71\alpha}{1 + \alpha} + \frac{71\alpha}{(1 + \alpha)} = 62.4$$

$$\text{Or } \frac{71 - 71\alpha + 71\alpha}{1 + \alpha} = 62.4$$

$$\text{Or } \frac{71}{1 + \alpha} = 62.4$$

Or

$$\frac{71}{62.4} = 1 + \alpha$$

$$\alpha = \frac{71}{62.4} - 1$$

$$\alpha = 0.138$$

Thus the fraction of chlorine dissociated into atoms is 0.138

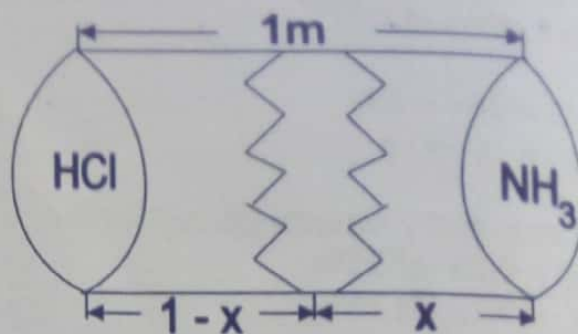
Qn. 61

Two pipes of cotton wool one sealed in ammonia and another in HCl were placed at opposite ends of 1m glass tube. After some times a white solid of ammonium chloride first appeared at one point inside the tube. At what distance the white solid appeared from the end where ammonia was placed?

Solution

- let the distance from ammonia to white solid be x .

i.e.



$$\begin{aligned} \text{Then } M_{r_1} &= \text{NH}_3 = 17 \text{ g mol}^{-1} \\ M_{r_2} &= \text{HCl} = 36.5 \text{ g mol}^{-1} \end{aligned}$$

Also,

$$\text{Velocity of NH}_3 = V_1$$

$$\text{Velocity of HCl} = V_2$$

From

$$\frac{V_1}{V_2} = \sqrt{\frac{M_{r_2}}{M_{r_1}}}$$

$$\frac{V_1}{V_2} = \sqrt{\frac{36.5}{17}}$$

$$\frac{V_1}{V_2} = 1.465$$

$$V_1 = 1.465V_2$$

Recall,

$$\text{Velocity} = \frac{\text{Distance}}{\text{Time}}$$

$$\text{For NH}_3, V_1 = \frac{x}{t_1}$$

$$t_1 = \frac{x}{V_1}$$

For HCl,

$$V_2 = \frac{1-x}{t_2}$$

$$t_2 = \frac{1-x}{V_2}$$

For white solid to be formed $t_1 = t_2$

i.e.

$$\frac{x}{V_1} = \frac{1-x}{V_2}$$

$$xV_2 = V_1 - V_1x$$

But $V_1 = 1.465V_2$

$$xV_2 = 1.465V_2 - 1.465V_2x$$

$$x = 1.465 - 1.465x$$

$$\frac{2.465x}{2.465} = \frac{1.465}{2.465}$$

$$x = 0.594m$$

Then the white solid will be formed at 0.594m away from NH_3 .

Note:

It must be noted that the rate of diffusion/effusion is constant at constant temperature. But if temperature changes the rate of diffusion or effusion also changes.

Recall

$$r = \frac{K}{\sqrt{\rho}}$$

But $\rho = \frac{PM_r}{RT}$

Then,

$$r = \frac{K}{\sqrt{PM_r/RT}}$$

For different rates of diffusion of the same gas

$$r_1 = K \sqrt{\frac{RT_1}{PM_r}}$$

Also,

$$r_2 = K \sqrt{\frac{RT_2}{PM_r}}$$

- Taking ratio of r_1 and r_2

$$\frac{r_1}{r_2} = \sqrt{\frac{T_1}{T_2}}$$

- In this case we are comparing the rates of diffusion of the same gas under different conditions of temperature.

Qn. 62

Calculate the ratio of rates of diffusion of a gas at $0^\circ C$ and $27^\circ C$.

Solution

Data

$$T_1 = 0 + 273K = 273K$$

$$T_2 = 27 + 273K = 300K$$

From,

$$\frac{r_1}{r_2} = \frac{273}{300}$$

$$\frac{r_1}{r_2} = 0.91 \text{ or } \frac{91}{100}$$

Then the ratio of rates of diffusion of a gas at $0^\circ C$ and $27^\circ C$ is 91:100.

THE KINETIC MOLECULAR THEORY OF GASES

- The gas laws help us to predict the behavior of gases, but they do not explain what happens at the molecular level to cause what happens at the molecular level to cause the changes we observe in the macroscopic world. For example, why does a gas expand on heating.
- In the 19th century, a number of physicists notably Ludwig Boltzmann and James Clerk Maxwell, found that the physical properties of gases can be explained in terms of the motion of individual molecules.
- This molecular movement is a form of energy, which we define as the capacity to do work or to produce change. In mechanics, work is defined as force times distance. Because energy can be measured as work, we can write.

$$\begin{aligned} \text{Energy} &= \text{Work done} \\ &= \text{Force} \times \text{distance} \end{aligned}$$

The joule (J) is the SI unit of energy

$$\begin{aligned} \text{i.e. } 1J &= 1\text{kgm}^2/\text{s}^2 \\ &= 1\text{Nm} \end{aligned}$$

Alternatively energy can be expressed in kilojoules (kJ)

i.e.

$$1\text{kJ} = 1000\text{J}$$

POSTULATES/ASSUMPTIONS OF KINETIC MOLECULAR THEORY OF GASES

- The kinetic molecular theory of gases attempt to explain the properties of an ideal gas. This model is based on speculation about the behavior of the individual gas particles (atoms or molecules) which can not be seen, hence it is said to provide a microscopic model of gases.
- The assumptions/postulates were developed by Clausium, Maxwell, Boltzmann and others. The basic postulates of the kinetic theory of gases are described below:-
 - (i) Gases consist of large number of very small particles (atoms or molecules). These particles in any gas are assumed to be solid and spherical.
 - (ii) Volume occupied by the molecule is negligible compared to the total volume of the gas (volume of the container).
 - (iii) Force that exist between the molecules is negligible.
 - (iv) Gaseous molecules are always in a random motion in a straight line. During the motion they collide with each other or with the wall of the container.
 - (v) When gaseous molecules collide with each other or with the wall of the vessel the collision is perfectly elastic i.e. No loss in kinetic energy.
 - (vi) The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas

$$\text{i.e. } KE_{av} \propto T$$

- (vii) The pressure exerted by a gas is due to the collisions of the particles with the wall of the container. The pressure exerted by a gas is equal to the average force per unit area which the molecule exert on the walls of the container.

EVIDENCES FOR THE ABOVE ASSUMPTIONS.

- **Assumption (i) and (ii)**
 - Actual volume of the molecules is negligible in comparison to the empty space between them because of very small particles which are far from one another.
- **Assumption (iii)**
 - There is no force of attraction between particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- **Assumption (v)**
 - Particles of a gas are always in constant and random motion (Brownian motion). If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- **Assumption (v)**
 - Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains the same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remain constant.
 - If there were loss in Kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.

Assumption (vi)

- At any particular time, different particles in the gas have different speeds and hence different kinetic energies. As the particles collide we expect their speed to change. Even if initial speed of all the particles was the same, the molecular collisions will disrupt this uniformity.
- Consequently the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy is directly proportional to the absolute temperature.

KINETIC GAS EQUATION

- Mathematical expression of kinetic molecular theory of gases is called kinetic gas equation and is expressed as

$$PV = \frac{1}{3} Nm\bar{u}^2$$

Where,

P = is the Pressure exerted by the gas

V = volume of the gas

m = mass of each particle of the gas

N = number of particles in total volume of the gas

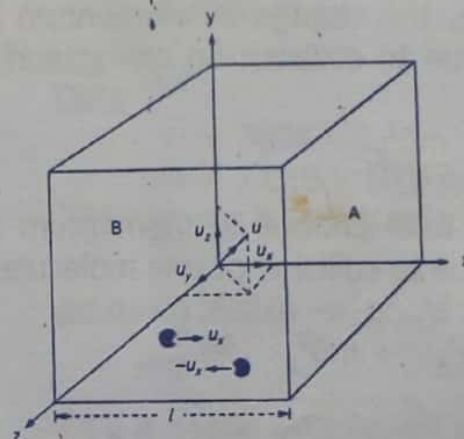
$\bar{u}^2$ = mean square speed of the gas molecule.

DERIVATION OF KINETIC GAS EQUATION

- To derive kinetic gas equation let us consider about N molecules of gas each having mass m which are enclosed in a container with sides measuring L cm.
- From the above postulates we know that gas molecules within a container move at different speeds.

- However, the speed (velocity u) of a particular molecule at any moment of time can be resolved into three components along the three mutual perpendicular axes of a vessel at right angles to each other.

- Let us see how to do this for a single molecule having a velocity u . The three velocity components of the molecule along the three axes, x , y and z are given as u_x , u_y and u_z .



- Thus the resultant mean square velocity $\bar{u}^2 = \bar{u}_x^2 + \bar{u}_y^2 + \bar{u}_z^2$
- This mean square velocity must be used because pressure is proportional to the square of molecular velocity.
- A molecule with mass m moves with velocity u along x direction on face A has momentum, (mu) .
- Because of the perfect elastic nature of the collisions, the momentum of the molecule before and after the impact along x - direction would be $+mu_x$ and $-mu_x$ respectively.
- Thus the change in momentum before and after the impact is given as, $mu_x - (-mu_x) = 2mu_x$
- For the molecule to experience another impact on the same face again it has to go to the opposite face and come back. Thus, the molecule has to travel a distance of $2L$ cm.

- Since the molecule experience many impacts in the vessel, then it is preferred to express change in momentum per time.

$$\text{i.e. } \frac{\Delta P}{\text{Time}} = \frac{2mu_x}{t}$$

$$\text{But } t = \frac{\text{distance}}{\text{velocity}} = \frac{2L}{u_x}$$

Then from above

$$\frac{\Delta P}{\text{Time}} = \frac{2m\bar{u}_x}{2L/u_x} = \frac{2m\bar{u}_x^2}{2L} = \frac{m\bar{u}_x^2}{L} = \text{Change in momentum per second}$$

- Like wise, the change in momentum per second due to collision on other surface given as

$$\frac{m\bar{u}_x^2}{L}$$

- Now, the total change in momentum per second due to collision of one molecule on two faces along x-axis is given as,

$$= \frac{m\bar{u}_x^2}{L} + \frac{m\bar{u}_x^2}{L}$$

$$= \frac{2m\bar{u}_x^2}{L}$$

- Similarly, the change in momentum due to collisions of the molecule on the surfaces y and z is given as

$$= \frac{2m\bar{u}_y^2}{L} \text{ and } \frac{2m\bar{u}_z^2}{L} \text{ respectively.}$$

- Thus, the total change in momentum per second on all the six faces along the three axes is given as,

$$\frac{2m\bar{u}_x^2}{L} + \frac{2m\bar{u}_y^2}{L} + \frac{2m\bar{u}_z^2}{L}$$

$$= \frac{2m}{L} (\bar{u}_x^2 + \bar{u}_y^2 + \bar{u}_z^2)$$

$$= \frac{2m\bar{u}^2}{L} \text{ as, } (\bar{u}_x^2 + \bar{u}_y^2 + \bar{u}_z^2 = \bar{u}^2)$$

- As there are N molecules of a gas each moving with a different velocity, the velocity of each molecules contributes to change in momentum per second on all the six faces along the three axes.

- Thus the total change of momentum per

second to N molecules is given as,

$$\frac{2Nm\bar{u}^2}{L}$$

- The change of momentum per second is termed as force, F.

$$F = \frac{2mN\bar{u}^2}{L}$$

- Now, pressure P is given as force per unit area

$$P = \frac{\text{Total force}}{\text{Total area}}$$

$$P = \frac{2mN\bar{u}^2}{L \times \text{area}}$$

- Since in a cubic vessel there are six wall surfaces, then,

$$\text{Area} = 6L^2$$

Then,

$$P = \frac{2mN\bar{u}^2}{L \times 6L^2}$$

$$P = \frac{mN\bar{u}^2}{3L^3}$$

- We know that $L^3 = \text{Volume, } V$. Then,

$$P = \frac{mN\bar{u}^2}{3V}$$

or

$$PV = \frac{1}{3}Nm\bar{u}^2$$

Kinetic gas equation

Note:

Though the above equation is derived for a cubic vessel, it is applicable for a vessel of any shape as the total volume is considered to be made up of a number of small cubes.

ROOT MEAN SQUARE SPEED/VELOCITY

Root mean square speed is the measure of the speed of particles in a gas that is most convenient for problem solving within the kinetic theory of gases. It is defined as the square root of the average velocity-squared of the molecules in a gas.

- Root mean square speed/velocity is ob-

ained form ideal gas equation and kinetic theory equation, thus,

$$PV = nRT = \frac{1}{3} Nm(\bar{u}^2)$$

$$\text{Or } 3RT = \frac{Nm(\bar{u}^2)}{n} \dots\dots\dots (i)$$

Since N is the number of molecules and m is the mass of each molecule, then Nm is the total mass of gas. Dividing total mass by the amount of substance gives molar mass.

i.e.

$$M = \frac{Nm}{n}$$

Substituting this value in equation one we have

$$3RT = M\bar{u}^2$$

$$\text{Or } \bar{u}^2 = \frac{3RT}{M}$$

$$\text{So that } u_{r.m.s} = \bar{u} = \sqrt{\frac{3RT}{M}} \dots\dots\dots (ii)$$

Generally,

$$u_{r.m.s} = \sqrt{\frac{3RT}{M}}$$

Where:- R = Ideal gas constant (8.314 Jmol⁻¹K⁻¹)
But 1J = 1Kgm².s⁻².

T = Temperature in Kelvin

M = Molar mass in kilograms.

The quantity $u_{r.m.s}$ is called root.mean-square (r.m.s) velocity because it is the square root of the mean square velocity.

The r.ms. velocity is directly proportional to the square root of temperature and inversely proportional to the square root of molar mass. Thus quadrupling the temperature of a given gas doubles the root

mean square velocity of the molecules.

Doubling this average velocity doubles the number of collisions between gas molecules and the walls of a container. It also doubles the impulse of each collision. Thus the pressure quadruples.

Qn. 63

Find the root mean velocity for (a)H₂ and (b) O₂ molecules at 27°C.

Solution

(a) For H₂

Data

$$T = 300K$$

$$M = 2.016 \times 10^{-3} \text{kgmol}^{-1}$$

$$R = 8.314 \text{kg.m}^2.\text{s}^{-2}$$

From

$$u_{r.m.s} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8.314 \text{kg.m}^2.\text{s}^{-2} \text{mol}^{-1}.\text{K}^{-1} \times 300K}{2.016 \times 10^{-3} \text{kg.mol}^{-1}}}$$

$$= 1.927 \times 10^3 \text{ms}^{-1}.$$

(b) For O₂

Data

$$T = 300K.$$

$$R = 8.314 \text{kgm}^2\text{s}^{-2}$$

$$M = 32 \times 10^{-3} \text{kgmol}^{-1}$$

From

$$u_{r.m.s} = \sqrt{\frac{3RT}{M}}$$

$$u_{r.m.s} = \sqrt{\frac{3 \times 8.314 \times 300 \text{kgm}^2\text{s}^{-1}\text{mol}^{-1}\text{K}^{-1}.\text{K}}{32 \times 10^{-3} \text{kgmol}^{-1}}}$$

$$u_{r.m.s} = 4.836 \times 10^2 \text{m/s}$$

Qn 64.

Calculate the root mean square speed of carbon dioxide molecules at 1000°C.

Solution

Data

$$M = 44 \times 10^{-3} \text{ kg mol}^{-1}$$

$$T = 1000 + 273 \text{ K}$$

$$R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

From

$$u_{r.m.s} = \sqrt{\frac{3RT}{M}}$$

$$u_{r.m.s} = \sqrt{\frac{3 \times 8.314 \times 1273 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1} \cdot \text{K}}{44 \times 10^{-3} \text{ kg mol}^{-1}}}$$

$$u_{r.m.s} = 849.5 \text{ m/s}$$

Qn. 65

Calculate the root mean square speed of oxygen gas molecules under S.T.P conditions. Density of oxygen at S.T.P is 1.429 g L^{-1} .

Solution

From

$$u_{r.m.s} = \sqrt{\frac{3RT}{M}}$$

But $PV = RT$, then,

$$u_{r.m.s} = \sqrt{\frac{3PV}{M}}$$

But $\frac{m}{V} = \rho$ then, $\frac{V}{M} = \frac{1}{\rho}$

Then,

$$u_{r.m.s} = \sqrt{\frac{3P}{\rho}}$$

- Standard pressure.

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa (Nm}^{-2}\text{)}$$

$$\text{But } (1 \text{ Nm}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2})$$

$$\text{Density, } \rho = 1.429 \text{ g/L}$$

$$= 1.429 \times 10^{-3} \text{ kg/10}^{-3} \text{ m}^3$$

$$= 1.429 \text{ kg.m}^3$$

From,

$$u_{r.m.s} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1.013 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}}{1.429 \text{ kg m}^{-3}}}$$

$$u_{r.m.s} = 461 \text{ ms}^{-1}$$

PROVING KINETIC GAS EQUATION FROM GAS LAWS

- One of the application of kinetic gas equation, to prove all gas laws derived or explained earlier

(i) PROOF FROM BOYLE'S LAW.

- Boyle's law states that "The volume of a fixed amount of a gas is inversely proportional to its pressure at constant temperature".

Mathematically

$$V \propto 1/P \text{ (Constant } T\text{)}$$

From kinetic gas equation

$$PV = \frac{1}{3} N m \bar{u}^2$$

$$\text{Or } PV = \frac{2}{3} \left(\frac{1}{2} N m \bar{u}^2 \right)$$

$$PV = \frac{2}{3} \times N \left(\frac{1}{2} m \bar{u}^2 \right)$$

Then,

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \bar{u}^2 \right)$$

- At a fixed temperature, the average kinetic energy of the molecule $\frac{1}{2} m \bar{u}^2$ remains constant. For a certain amount of a gas, the number of molecules (N) is also constant. Thus, for a certain amount of a gas, at any fixed temperature.

$$PV = \frac{2}{3} \times \text{constant} = \text{constant } K.$$

Then, $PV = K$

Or

$$V = \frac{K}{P}$$

Then,

$$\boxed{V \propto 1/P} \text{ This is the statement of Boyles law.}$$

(ii) PROOF FROM CHARLES' LAW

Charles' laws states that "Volume of a fixed mass of a gas at constant pressure is directly

proportional to absolute temperature"

i.e.

$$V \propto T \text{ (Constant P)}$$

From Kinetic gas equation

$$PV = \frac{1}{3} Nm\bar{u}^2$$

$$PV = \frac{2}{3} N (\frac{1}{2} m\bar{u}^2)$$

- But we have seen that $K.E_{av} \propto T$

i.e.

$$\frac{1}{2} m\bar{u}^2 \propto T$$

Hence for a fixed amount of a gas under constant pressure

$$V = \frac{2}{3} \frac{N}{P} \times T \quad \text{But } \frac{2}{3} \frac{N}{P} = \text{Constant } K.$$

Then,

$$V = KT$$

Then,

$$V \propto T$$

Or $\frac{V}{T} = \text{Constant}$

- This is what the Charles' law states.

(iii) PROOF FROM IDEAL GAS EQUATION

From ideal gas equation

$$PV = nRT$$

Also kinetic gas equation

$$PV = \frac{1}{3} Nm\bar{u}^2$$

Or

$$PV = \frac{2}{3} N (\frac{1}{2} m\bar{u}^2)$$

- but we know that average kinetic energy $\frac{1}{2} m\bar{u}^2$ is directly proportional to absolute temperature.

i.e.

$$\frac{1}{2} m\bar{u}^2 \propto T \text{ then}$$

$$PV = \frac{2}{3} N.T$$

- But for any gas $N \propto n$ and $\frac{2}{3}$ remain constant for a fixed amount of gas.

i.e.

$$PV = \text{Constant} \times n \times T$$

$$PV = KnT$$

Where K is constant called universal gas constant denoted by R. then

$$PV = nRT$$

This is an ideal gas equation.

(iv) PROOF FROM GRAHAM'S LAW.

Graham's law states that "The rate of diffusion is inversely proportional to the square root of its density".

Mathematically,

$$r \propto \frac{1}{\sqrt{\rho}}$$

- From kinetic theory

$$PV = \frac{1}{3} Nm\bar{u}^2$$

Or

$$\bar{u}^2 = \frac{3PV}{Nm}$$

Where Nm the total mass of the molecules in volume V of the gas. Therefore the density of the gas (ρ) is expressed as,

$$\rho = \frac{Nm}{V}$$

Then,

$$\bar{u}^2 = \frac{3P}{\rho}$$

Or

$$u_{r.m.s} = \sqrt{\bar{u}^2} = \sqrt{\frac{3P}{\rho}}$$

Thus,

$$\text{R.m.s speed} = \sqrt{\frac{3P}{\rho}}$$

- But root mean square speed lies linearly to rate.

Then,

$$\text{R.m.s speed} \propto \text{Rate.}$$

Then,

$$r \propto \frac{1}{\sqrt{\rho}}$$

If pressure is constant. Hence Graham's law is proved.

(v) PROOF FROM AVOGADRO'S LAW

- Avogadro's law states that "At the same temperature and pressure, equal volumes of all the gases contain equal number of molecules.
- Consider equal volumes of two gases kept at the same pressure and temperature,

Let,

m_1 = Mass of a molecule of the first gas

m_2 = Mass of a molecule of the second gas

N_1 = Number of molecules of the first gas

N_2 = Number of molecules of the second gas

P = Common pressure of the two gases

V = Common volume of the two gases.

From Kinetic gas equation,

$$PV = \frac{1}{3}Nm\bar{u}^2$$

For gas 1,

$$PV = \frac{1}{3}N_1m_1\bar{u}_1^2$$

For gas 2

$$PV = \frac{1}{3}N_2m_2\bar{u}_2^2$$

Where $\bar{u}_1$ and $\bar{u}_2$ are r.m.s speeds of the molecules of the first and the second gas respectively. Thus,

$$N_1m_1\bar{u}_1^2 = N_2m_2\bar{u}_2^2 \dots\dots\dots(i)$$

- As the temperatures of the gases are the same, the average kinetic energy per molecule is the same for the two gases.

i.e.

$$\frac{1}{2}m_1\bar{u}_1^2 = \frac{1}{2}m_2\bar{u}_2^2 \dots\dots\dots(ii)$$

Now from (i) and (ii)

$N_1 = N_2$ which proved Avogadro's law.

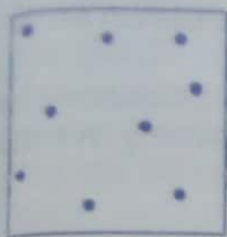
DEVIATION FROM IDEAL BEHAVIOUR (Concept of Real gases)

- A gas which obeys the ideal gas equation ($PV = nRT$) at all temperatures and pressures is called an **ideal gas** or **perfect gas**. Actually, none of the known gases obey the ideal gas equation under all conditions of temperatures and pressures.
- The gases which do not obey the ideal gas equation are called **real gases** or **imperfect gases**.
- The behavior of real gases usually agrees with the predictions of the ideal gas equations to within $\pm 5\%$ at normal temperatures and pressures. At low temperatures or high pressures, real gases deviate significantly from ideal gas behavior.
- In 1873, while searching for a way to link the behavior of liquids and gases, the Dutch physicist Johannes van der Waal developed an explanation for these deviation and an equation that was able to fit the behavior of real gases over a much wide range of pressures.
- Van der Waals realized that two of the assumptions of the kinetic molecular theory of gases were questionable,
 - (i) The real volume of the gas molecules is negligible when compared to the volume of the container.
 - (ii) There are no forces of attraction or repulsion between the gas molecules.

- Hence van der Waal suggested the following corrections.

- The gas molecules possess finite volume and hence should not be neglected. It is especially true at high pressures and low temperatures and should be accounted for.
- In case of real gases, both the force of attraction as well as repulsion operate between gas molecules.

Note: If the gases obey the kinetic theory of gases, then they can not be compressed since the attraction between the gas molecules is negligible.



Ideal Theory assumes that all of this space is available for the molecules to move around in...



...but in fact, only this amount is available, because the rest is taken up by the molecules themselves.

APPLICABILITY OF IDEAL GAS EQUATION

Is the condition in which ideal gas equation is true and hence can be applied.

- Hence applicability of ideal gas equation is at **low pressure** and **high temperature**.
- All gases will behave ideally if subjected at low pressure and high temperature.
- But if the gases are subjected at high pressure and low temperature they deviate from ideal gas behavior, why?
- This is because at high pressure and low temperature, the volume of the gas becomes small and molecules come close to each other.
- Under this condition, the attractive force between the molecules become operative. When volume becomes so small gases collide and liquefy. Ideal gas equation is applied only for gases and not liquids.

Note:

For each gas there is a characteristic temperature called the critical temperature, above which it is impossible to liquefy the gas no matter how much pressure is applied.

Critical Temperature (T_c): is the highest temperature at which a gas can be liquefied by increasing pressure.

- The pressure corresponding to the critical temperature is called critical pressure.

Critical Pressure (P_c)

Is the minimum pressure required to liquefy a gas at its critical temperature.

The volume per mole of a gas at its critical temperature and critical pressure is called

critical volume.

- These constants, critical temperature (T_c), critical pressure (P_c) and critical volume (V_c) are called Critical Constants of the gas. The value of T_c , P_c and V_c are constant for certain gas and they differ from one gas to another.

VAN DER WAAL EQUATION (Equation for Real gases)

- In deriving equation for real gases, van der Waal modified the ideal gas equation. This modification is done based on,
 - Volume correction
 - Pressure correction

(i) VOLUME CORRECTION

- The volume available for the gas molecules is less than the volume of the container, V .
- If b is the volume of one mole of gas molecule, then total volume of n moles of gas molecules will be nb . Thus the available volume for the molecules to move is obtained by subtracting volume of n -moles of gas, nb from the volume of the container.

i.e.

$$\text{Available volume} = V - nb$$

Where " b " is a constant characteristic of a gas.

- The ideal gas equation can be written after correcting this as

$$P(V - nb) = nRT$$

(ii) PRESSURE CORRECTION

- The pressure of the real gas is less than the expected pressure due to attractions between the molecules. These attractions slows down the motion of gas molecules and result in
 - Reduction of frequency of collisions over the walls.
 - Reduction in the force with which the molecules strike the walls.

Hence,

$$P_{\text{ideal}} = P_{\text{real}} + P_r$$

Where

$$P_r = \text{Reduction in pressure}$$

- The pressure reduced is found to depend upon the number of particles per unit volume of a gas. This means that reduction in pres-

sure is 'proportional to the square of molar concentration, n/v . Thus,

The reduction in pressure (P_r) $\propto n/v \times n/v$

One factor for reduction in frequency of collisions and the second factor for reduction is strength of their impulses on the walls.

Then from,

$$P_r \propto (n/v)^2$$

$$P_r = \frac{an^2}{V^2}$$

Where,

"a" is a proportionality constant characteristic of a gas

Therefore from,

$$P(V - nb) = nRT \text{ becomes}$$

$$P + P_r(V - nb) = nRT$$

$$\text{Or } P + \frac{an^2}{V^2}(V - nb) = nRT$$

$$P_r = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

- For one mole of a gas, the equation can be written as,

$$P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

Vander-waal Equation

Where

V_m = Volume occupied by one mole of a real gas

Remember that:

P = observed pressure of the real gas.

Whereas,

$$\left(P + \frac{an^2}{V^2} \right) = \text{Pressure corrected for ideal gas}$$

V = Volume occupied by the real gas and is equal to the volume of the container.

$V - nb$ = Available volume for gas molecules.

UNITS OF VAN DER WAAL CONSTANTS "a" AND "b"

- The units of "a" and "b" can be obtained from one of the steps used in deriving this equation

(i) Van der waal constant "a"

- The van der waal constant "a" is obtained from

$$P_r \propto (n/v)^2$$

Or

$$P_r = \frac{an^2}{V^2}$$

Multiply by V^2 on both sides we get,

$$P_r V^2 = an^2$$

Make a the subject

$$a = \frac{P_r V^2}{n^2}$$

- Now if pressure is measured in atm, and volume in litres then,

$$a = \frac{P_r (\text{atm})}{n^2 (\text{mol}^2)} \cdot V^2 (\text{L}^2) = \frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}$$

- Then units of "a" constant is $\text{atm} \cdot \text{L}^2 \text{mol}^{-2}$

(ii) Vander waal constant "b"

- The van der waal constant b is obtained from,

$$V - nb$$

Make b the subject

$$b = \frac{V}{n}$$

- Now if volume is measured in liters, then

$$b = \frac{V(\text{L})}{n(\text{Mol})}$$

$$b = \text{L} \cdot \text{Mol}^{-1}$$

Then units of b constant is $\text{L} \cdot \text{mol}^{-1}$

Significance of Van der - waal constants "a" and "b".

- The Van der - Waal 'a' is a measure of inter-molecular attraction therefore the value of 'a' reflects the tendency of the gas to liquefy. The gas having large value of 'a' will liquefy easily.
- The Van der - Waal constant 'b' is a measure of close packed molecular volume. Thus molecule of a gas having greater value of 'b' has bigger size.

BEHAVIOUR OF REAL GASES (Concept of compressibility factor)

- A gas is said to show deviation from ideal behavior when the product of the observed pressure and volume ($P \times V$) is lower or higher than that expected from the ideal gas equation.
- Thus for a gas showing deviations from ideal behaviour

$$(PV)_{\text{observed}} < nRT$$

Or

$$(PV)_{\text{observed}} > nRT$$

- Then to describe the behaviour of real gases, the ideal gas equation should be modified. This is conveniently done by writing the ideal gas equation in the form

$$PV = Z nRT$$

Or

$$Z = \frac{PV}{nRT}$$

Where Z can have a value of one, less than one or more than one. The factor Z is called compressibility factor, which is the ratio of PV to nRT .

- Depending upon the value of Z , the following three cases become possible.

Case 1:

When $Z = 1$, then, $PV = nRT$ the gas shows an ideal gas behaviour. For an ideal gas $Z = 1$ under all conditions of temperature and pressure.

Case 2

When $Z < 1$, the observed PV value is less than the value for an ideal gas i.e. Gas is more compressible than an ideal gas. Thus, the gas shows negative deviation when $Z < 1$.

Case 3

When $Z > 1$ the observed PV value is higher than the value for an ideal gas. i.e. Gas is less compressible than an ideal gas. Thus the gas shows positive deviation when $Z > 1$.

- Thus we see that compressibility factor Z can account for the behavior of real gases. The extent of departure from the value of 1 for Z , therefore, can be taken as a measure of deviations shown by a gas.
- Compressibility factor Z can also be obtained as a ratio of volume of real gas, V_{real} to the ideal volume of that gas, V_{perfect} calculated by ideal gas equation

i.e.

$$Z = \frac{PV_{\text{real}}}{nRT}$$

- But from ideal gas equation

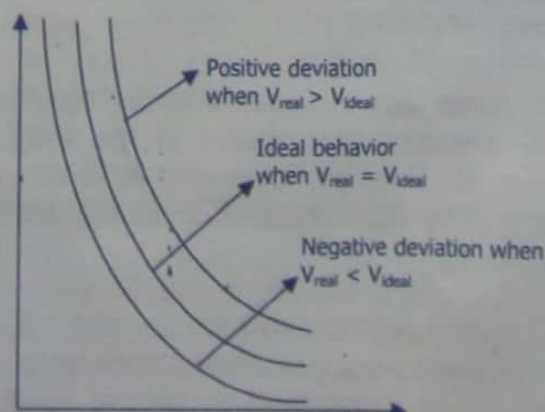
$$PV_{\text{perfect}} = nRT$$

Or

$$V_{\text{perfect}} = \frac{nRT}{P}$$

Therefore,

$$Z = \frac{PV_{\text{real}}}{nRT} = \frac{V_{\text{real}}}{V_{\text{perfect}}}$$



* For ideal or perfect gases, the compressibility factor, $Z = 1$

* But for real, $Z \neq 1$

Case I: If $Z > 1$

- $V_{\text{real}} > V_{\text{ideal}}$
- The repulsion forces becomes more significant than the attractive forces.
- The gas can not be compressed easily
- Usually the $Z > 1$ for so called permanent gases like He, H_2

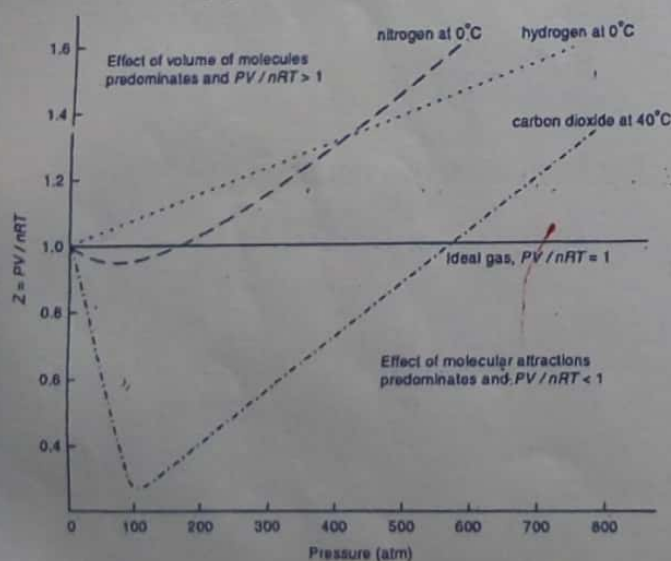
Case II: If $Z < 1$ ideal

- $V_{\text{real}} < V_{\text{ideal}}$
- The attractive forces are more significant than the repulsive forces
- The gas can be liquefied easily
- Usually the $Z < 1$ for gases like NH_3 , CO_2 and SO_2 .

Note:

The extent of deviations shown by a gas depend upon both temperature and pressure.

AMARGAT CURVE TO SHOW PLOT OF Z Vs P FOR SEVERAL GASES



EXPLANATION FROM THE GRAPH

- For hydrogen and helium (not shown in the plot) gases, Z is greater than one at all pressures.
- For gases like, nitrogen and carbon dioxide and methane (not shown in the plot) the value of Z is less than one at lower pressures, and greater than one at higher pressures.
- All gases tend to approach a value $Z = 1$ when pressure approaches a value zero. This means, all gases tend to behave ideally at very low pressures.

EXPLANATION OF DEVIATIONS UNDER DIFFERENT CONDITIONS USING VANDER WAAL CONSTANTS "a" AND "b"

At low pressure

- Since V is large and therefore " b " is negligible compared to V , the van der Waal equation for one mole of a gas is reduced to,

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V}$$

- Note that $V = V_m = \text{Molar volume}$
- Therefore; $PV < RT$ at low pressures. This is the reason for decrease in the Z value at low pressures.

Note:

By dividing with RT on each side, the above equation can be written as,

$$\frac{PV}{RT} = 1 - \frac{a}{RTV}$$

Or

$$Z = 1 - \frac{a}{RTV}$$

At very low pressures

- Since V is very large and therefore both b and a/V^2 values become negligible. Hence the van der Waal equation for one mole of gas is reduced to:

$$PV = RT$$

- Therefore, at very low pressures all the gases obey ideal gas equation.

At high pressures

- Since the volume occupied by the gas (V) is small, the value of " b " can not be neglected. Although a/V^2 is also large its value may be neglected in comparison with very high value of P . Hence the Van der Waal equation is reduced to

$$P(V - b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

Therefore, at high pressure, $PV > RT$. This explains the increase value of Z .

Note:

By dividing with RT on each side, the above equation can be written as

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

Or

$$Z = 1 + \frac{Pb}{RT}$$

At high temperature.

In this case, V is very large and attractions, are negligible. Hence both b and a/v^2 are negligible. This reduces the Van der Waal equation to

$$PV = RT$$

FOR H_2 AND He GASES

Since the actual volume of these gases molecules is very small, the intermolecular forces of attraction are very small i.e. a/v^2 can be ignored. Thus the Van der Waal equation can be reduced to.

$$P(V - b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

Therefore for H_2 and He gases, $PV > RT$. Hence for these gases, the Z value is always greater than one as evident from the graph.

Note:

For each gas there is a fixed temperature at which the gas behaves like an ideal gas over an appreciable range of pressure.

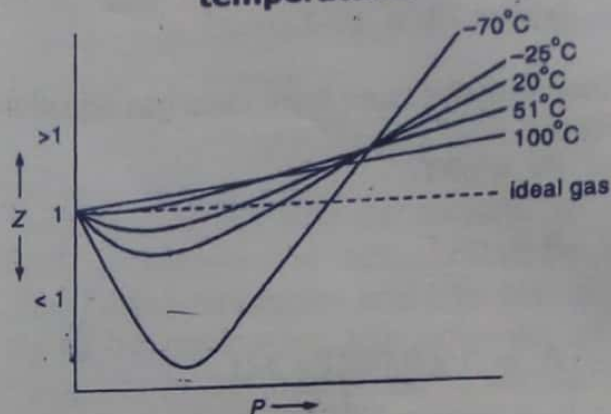
The temperature at which a gas behaves as an ideal gas over a wide range of pressure is called its Boyle's temperature (T_B)

Thus it appears that if a gas is below its Boyle's temperature ($T < T_B$) it would show negative deviation i.e. $Z < 1$ at least in the beginning.

- On the other hand if a gas is held at a temperature above its Boyle's temperature ($T > T_B$), then the gas shows positive deviation i.e. $Z > 1$ at all pressures.

- Of course if the gas is held at its Boyle's temperature ($T = T_B$) it will behave like an ideal gas, ($Z = 1$) over a wide range of pressure.

Consider the Z Vs P plots for N_2 at various temperature.



- From the graph above it appears that
 - i) At 51°C , nitrogen behaves as an ideal gas. Then 51°C is the Boyle's temperature of N_2 .
 - ii) At temperature below 51°C (when $T < T_B$) N_2 shows negative deviations at least in the starting portion of the curve
 - iii) At temperature above 51°C (when $T > T_B$), N_2 shows positive deviation at all pressures.
- The behaviour of H_2 and He which show positive deviations at all pressures can be explained in terms of their very low Boyle's temperatures.
- The Boyle's temperature of hydrogen and helium are -165°C and -240°C respectively. So when measurements are made at nearly room temperature, then the gases are at temperatures much above their Boyle's temperatures. As a result, Z vs P plots for H_2 and He show positive deviation at all pressures.

EXAMPLE OF PROBLEMS ON REAL GASES

Qn. 66:

One mole of carbon dioxide is found to occupy volume of 1.32L at 48°C . Calculate the pressure that would have been expected from :-

- i) Ideal gas equation

- ii) Van der Waal's equation given that a and b constants are $3.6 \text{ L}^2 \text{ atm mol}^{-2}$ and $4.28 \times 10^{-2} \text{ atm mol}^{-1}$ respectively.

Solution

Data

$$\begin{aligned} n &= 1 \text{ mol} \\ V &= 1.32 \text{ L} \\ T &= 48 + 273 \text{ K} = 321 \text{ K} \\ a &= 3.6 \text{ L}^2 \text{ atm mol}^{-2} \\ b &= 4.28 \times 10^{-2} \text{ L mol}^{-1} \end{aligned}$$

- (i) Required: Pressure from ideal gas equation
From;

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{1 \times 0.0821 \times 321}{1.32}$$

$$P = 19.97 \text{ atm.}$$

- (ii) Required: Pressure from van der waal equation

From,

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$P + \frac{a}{V^2} = \frac{RT}{V - b}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$P = \frac{0.0821 \times 321}{1.32 - 4.28 \times 10^{-2}} - \frac{3.6}{(1.32)^2}$$

$$P = 18.56 \text{ atm}$$

Qn. 67

Using Van der Waal equation, Calculate the constant " a " when two moles of a gas confined in a 4L flask exert a pressure of 11atm at 300K. The value of " b " is 0.05 L mol^{-1} .

Solution

Data

$$\begin{aligned} n &= 2 \text{ mol} \\ V &= 4 \text{ L} \\ P &= 11 \text{ atm} \end{aligned}$$

$$\begin{aligned} T &= 300 \text{ K} \\ b &= 0.05 \text{ L mol}^{-1} \end{aligned}$$

Solution

From,

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$P + \frac{an^2}{V^2} = \frac{nRT}{V - nb}$$

$$\frac{an^2}{V^2} = \frac{nRT}{V - nb} - P$$

$$\frac{an^2}{V^2} = \left(\frac{2 \text{ mol} \times 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{4 \text{ L} - (2 \text{ mol} \times 0.05 \text{ L mol}^{-1})} \right) - 11 \text{ atm}$$

$$\frac{an^2}{V^2} = \frac{1.631 \text{ mol atm L mol}^{-1} \text{ K}^{-1} \cdot \text{K atm}}{\text{L}^2}$$

$$V^2 \cdot \frac{an^2}{V^2} = 1.631 \text{ L}^{-1} \text{ atm} \times V^2$$

$$an^2 = 1.631 \text{ L}^{-1} \text{ atm} \times 4^2 \text{ L}^2$$

$$a = \frac{1.631 \text{ L}^{-1} \text{ atm} \times 4^2 \text{ L}^2}{2^2 \text{ mol}^2 \text{ L}^{-2}}$$

$$a = 6.524 \text{ atm mol}^{-2} \cdot \text{L}^{-2}$$

Qn. 68

Calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the Van der Waal equation if 3.5 moles of NH_3 occupy 5.2L at 47°C given a and b constants for ammonia are $4.17 \text{ atm L}^2 \text{ mol}^{-2}$ and $0.0371 \text{ L mol}^{-1}$.

Solution

Data

$$\begin{aligned} V &= 5.2 \text{ L} \\ T &= (47 + 273) \text{ K} = 320 \text{ K} \\ n &= 3.5 \text{ mol} \end{aligned}$$

- (a) pressure from ideal gas equation

From,

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{(3.5 \text{ mol})(0.0821 \text{ Latm.K}^{-1} \text{ mol})(320 \text{ K})}{5.2 \text{ L}}$$

$$P = 17.7 \text{ atm.}$$

(b) Req: Pressure from Van der Waal equation

Given,

$$a = 4.17 \text{ atmL}^2 \text{ mol}^{-2}$$

$$b = 0.0371 \text{ L/mol.}$$

From,

$$P + \frac{an^2}{V^2} = \frac{nRT}{V - nb}$$

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$P = \frac{(3.5 \times 0.0821 \times 320)}{5.2 - (3.5 \times 0.037)} - \frac{4.17 \times (3.5)^2}{(5.2)^2}$$

$$P = 16.2 \text{ atm}$$

Qn 69:

Predict which of the substances, NH_3 , N_2 , CH_2Cl_2 , Cl_2 , CCl_4 has

- The smallest Van der Waal "a" constant
- The largest "b" constant.

Solution

(i) N_2 .

The value of the van der waals constant, "a" of a given gaseous substance depends on the strength of attractions between its component molecules. Molecules experiencing the weakest attractive forces will have the smallest "a" constant while those with the strongest attractive forces will have the largest "a" values.

Of the molecules NH_3 , N_2 , CH_2Cl_2 , Cl_2 and CCl_4 alone have non-polar bonds between their component atoms. This results in weaker attractions between molecules, so N_2 and Cl_2 will have the smallest "a" values.

The remaining molecules all have polar bonds between their component atoms and in the case of NH_3 , hydrogen bonds between molecules. These are factors that lead to increased "a" constants. As N_2 molecule is smaller than the Cl_2 molecule and therefore has less electrons present, the attractive forces between N_2 molecules will be weaker than those between Cl_2 molecules and N_2 will have the smallest "a" constant.

(ii) CCl_4 .

The value of the Van der Waal's "b" constant is merely the actual volume of a mole of the molecules and this can be deduced by comparing the volumes of the molecules in the list. Small molecular volume results in small "b" values and large molecular volume corresponds to a large b constant. From the compounds in the list, CCl_4 is the largest and so it will have the greatest "b" constant.

Qn. 70

Real gases do not behave ideally

- State the two major assumptions which are made for ideal gas behaviour.
- (a) State the physical conditions under which real gases approach ideal gas behaviour and,
- (b) Explain those conditions in terms of the two assumptions in (i) above.

VAPOUR DENSITY

Vapour density is the density of a vapour relative to that of hydrogen. It may be defined as mass of a certain volume of a substance divided by mass of the same volume of hydrogen.

i.e.

$$\text{Vapour density} = \frac{\text{Mass of } n \text{ molecules of gas}}{\text{Mass of } n \text{ molecules of hydrogen}}$$

Therefore,

$$\text{Vapour density} = \frac{\text{Molar mass of a gas}}{\text{Molar mass of hydrogen}}$$

$$\text{Vapour density} = \frac{\text{Molar mass of a gas}}{2.016}$$

$$\text{Vapour density} = 1/2 \times \text{Molar mass of a gas}$$

Thus,

$$\text{Molar mass} = 2 \times \text{Vapour density}$$

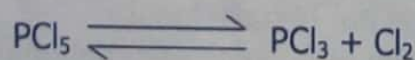
i.e.

$$\boxed{Mr = 2VD}$$

EFFECT OF DISSOCIATION ON RELATIVE MOLAR MASS OF A GAS

- **Dissociation:** -Is the splitting of either solids, liquids or a gas into smaller particles. (or ions).
- Extent of dissociation is determined by the degree of dissociation or (ionization).
- **Degree of dissociation:** Is the fraction or percentage of the original substance which has dissociated.
- Since dissociation tend to reduce the size of original substance hence tend to affect the molar mass of any substance.

i.e.



$$\begin{array}{cccc} (100\%)1 & 0 & 0 & t = 0 \\ 1 - \alpha & \alpha & \alpha & t = t \end{array}$$

$$\text{Total moles before dissociation } n_1 = 1$$

$$\text{Total moles after dissociation } n_2 = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

But ,

$$\text{Mass before dissociation } (n_1 Mr_1) = \text{Mass after dissociation } (n_2 Mr_2)$$

$$\text{i.e. } Mr_1 = (1 + \alpha) Mr_2$$

$$\text{Or } \frac{Mr_1}{Mr_2} = 1 + \alpha$$

$$\frac{Mr_1 - 1}{Mr_2} = \alpha$$

$$\boxed{\alpha = \frac{Mr_1 - 1}{Mr_2}}$$

But

$$\text{Molar mass} = 2 \times \text{vapour density}$$

i.e.

$$Mr = 2VD$$

Then,

$$\boxed{\alpha = \frac{VD_1 - 1}{VD_2}}$$

Where,

Mr_1 = Molar mass before dissociation (Actual Mr)

Mr_2 = Molar mass after dissociation (Apparent Mr)

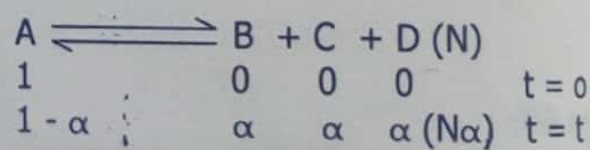
VD_1 = Vapour density before dissociation (Actual V.D).

VD_2 = Vapour density after dissociation (Apparent V.D)

Note:

The above formula applies only when one mole splits to give 2 moles. Now consider when one mole of A splits to give N - moles (particles).

i.e.



Then

$$\text{Total moles before dissociation } n_1 = 1$$

$$\begin{aligned} \text{Total moles after dissociation } n_2 &= 1 - \alpha + N\alpha \\ &= 1 + N\alpha - \alpha \\ &= 1 + \alpha(N-1) \end{aligned}$$

Now,

$$\text{Mass before dissociation } (n_1 Mr_1) = \text{Mass after dissociation } (n_2 Mr_2)$$

i.e.

$$Mr_1 = 1 + \alpha(N-1) Mr_2$$

$$Mr_1 - 1 = \alpha(N-1) Mr_2$$

$$\frac{Mr_1 - 1}{Mr_2} = \alpha(N-1)$$

$$\frac{Mr_1 - Mr_2}{Mr_2(N-1)} = \alpha$$

Then

$$\alpha = \frac{Mr_1 - Mr_2}{Mr_2(N - 1)}$$

Or

$$\alpha = \frac{VD_1 - VD_2}{VD_2(N - 1)}$$

Where

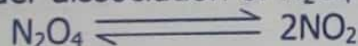
N = Is the number of particles formed after dissociation on one mole of a given substance.

Qn. 71

The relative vapour density of partially dissociated dinitrogen tetraoxide at 26°C is 38.3. Find the degree of dissociation (N = 14, O = 16)

Solution

Consider dissociation of N_2O_4



Data

V.D after dissociation = 38.3

V.D before dissociation = $\frac{Mr_1}{2} = \frac{92}{2} = 46$

From

$$\alpha = \frac{VD_1 - 1}{VD_2}$$

$$\alpha = \frac{46 - 1}{38.3}$$

$$\alpha = 0.2$$

Qn. 72

At 500C and 197.3Kpa, 1dm³ of partially dissociated N_2O_4 was found to have mass of 2.5g. What is the degree of dissociation of under these conditions.

Solution

Data

Mass = 2.5g

Volume = 1dm³

Temperature = 773K

Pressure = 197Kpa

From Ideal gas equation

$$PV = nRT$$

$$PV = \frac{mRT}{Mr}$$

$$Mr = \frac{mRT}{PV}$$

$$Mr = \frac{2.5 \times 8.314 \times 773}{197.3 \times 10^3 \times 1 \times 10^{-3}}$$

$$Mr = \frac{2.5 \times 8.314 \times 773}{197.3}$$

$$Mr = 81.43 \text{ gmol}^{-1}$$

- This molar mass (81.43gmol⁻¹) is the apparent Mr. due to the fact that it is obtained after dissociation.

i.e.

$$Mr_1 \text{ of } N_2O_4 = 92 \text{ mol}^{-1}$$

$$Mr_2 \text{ of } N_2O_4 = 81.43 \text{ gmol}^{-1}$$

Also ,



$$N = 2$$

From

$$\alpha = \frac{Mr_1 - 1}{Mr_2}$$

$$\alpha = \frac{92}{81.43} - 1$$

$$\alpha = 0.13$$

Qn. 73

At 60°C 1dm³ of N_2O_4 gas weighed 2.58g under pressure of 1.01 x 10⁵ Pa. Find the degree of dissociation of N_2O_4 and its Kp.

Solution

$$m = 2.585 \text{ g}$$

$$T = 60 + 2.73 = 333 \text{ K}$$

$$P = 1.01 \times 10^5 \text{ Pa.}$$

$$V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

From

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

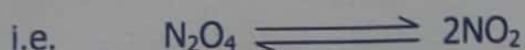
$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{2.585 \times 8.314 \times 333}{1.01 \times 10^5 \times 10^{-3}}$$

$$M_r = 70.86 \text{ g mol}^{-1}$$

Then, apparent $M_r = 70.86$

Actual $M_r = 92$



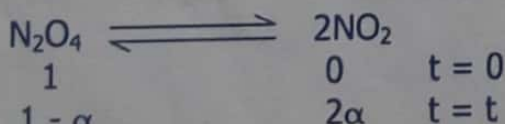
From

$$\alpha = \frac{M_{r1}}{M_{r2}} - 1$$

$$\alpha = \frac{92}{70.86} - 1$$

$$\alpha = 0.298$$

Consider the reaction below



Conc at eq $\frac{1-\alpha}{V}$

$\frac{2\alpha}{V}$

Then from

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$K_c = \frac{(2\alpha/V)^2}{1-\alpha/V}$$

$$K_c = \frac{(2\alpha)^2}{V^2(1-\alpha/V)}$$

$$K_c = \frac{(2\alpha)^2}{V} \div 1-\alpha$$

But $V = 1 \text{ dm}^3$

$$K_c = \frac{(2\alpha)^2}{1-\alpha} = \frac{4\alpha^2}{1-\alpha}$$

But $\alpha = 0.298$

$$K_c = \frac{4(0.298)^2}{1-0.298}$$

$$K_c = 0.51 \text{ mol dm}^{-3}$$

From

$$K_p = K_c(RT)^{m-n}$$

$$K_p = K_c(RT)^{2-1}$$

$$K_p = K_c RT$$

$$K_p = 0.51 \text{ mol dm}^{-3} \times 0.0821 \text{ atm dm}^3 \cdot \text{mol}^{-1} \text{K}^{-1} \times 333$$

$$K_p = 13.94 \text{ atm}$$

Qn 74.

20.85g of PCl_5 were allowed to vapourize in 5 dm^3 vessel at 175°C and a pressure of $1.04 \times 10^5 \text{ Nm}^{-2}$ develops. Calculate the degree of dissociation of PCl_5 . ($P = 31, \text{Cl} = 35.5$)

Solution

Data

$$m = 20.85 \text{ g}$$

$$V = 5 \times 10^{-3} \text{ m}^3$$

$$T = 175 + 273 = 448 \text{ K}$$

$$P = 1.04 \times 10^5 \text{ Nm}^{-2}$$

From

$$PV = nRT$$

$$PV = \frac{mRT}{M_r}$$

$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{20.85 \times 8.314 \times 44.8}{1.04 \times 10^5 \times 5 \times 10^{-3}}$$

$$M_r = 149.35 \text{ g mol}^{-1}$$

Then,

$$\text{Actual } M_r (M_{r1}) = 208.5 \text{ g mol}^{-1}$$

$$\text{Apparent } M_r (M_{r2}) = 149.35 \text{ g mol}^{-1}$$

From

$$\alpha = \frac{Mr_1 - 1}{Mr_2}$$

$$\alpha = \frac{208.5}{149.35} - 1$$

$$\alpha = 0.4$$

Thus, the degree of dissociation is 0.4

Qn. 75

At certain temperature under identical conditions volumes of O_2 and N_2O_4 diffusing from an apparatus to the ratio of 3:2. Calculate the degree of dissociation of N_2O_4 at this temperature.

Solution

Let us find the apparent molar mass of N_2O_4

From

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

Where

r_1 = rate of diffusion of O_2

r_2 = rate of diffusion of N_2O_4

Mr_1 = Molar mass of oxygen

Mr_2 = Apparent molar mass of N_2O_4

Then from above

$$\frac{r_1}{r_2} = \sqrt{\frac{Mr_2}{Mr_1}}$$

$$\frac{3}{2} = \sqrt{\frac{Mr_2}{32}}$$

$$\left(\frac{3}{2}\right)^2 = \frac{Mr_2}{32}$$

$$Mr_2 = 32 \times \left(\frac{3}{2}\right)^2$$

$$Mr_2 = 72 \text{ g mol}^{-1}$$

Then apparent molar mass of N_2O_4 is 72 g mol^{-1} and actual molar mass of N_2O_4 is 92 g mol^{-1}

$$\alpha = \frac{Mr_1 - 1}{Mr_2}$$

From

$$\alpha = \frac{92}{72} - 1$$

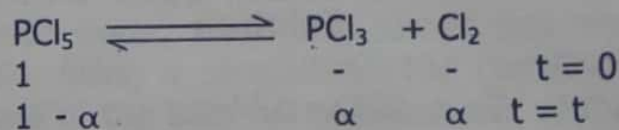
$$\alpha = 0.28$$

Qn. 76

If phosphorus pentachloride is 20% dissociated at a certain temperature, calculate the vapour density of the equilibrium mixture of the pentachloride, trichloride and chlorine at this temperature.

Solution

Consider the dissociation reaction



Then total particles (molecules) after dissociation
 $= 1 - \alpha + \alpha + \alpha$
 $= 1 + \alpha$

Then, mass before dissociation

$$n_1 Mr_1 = \text{Mass after diss} = n_2 Mr_2$$

$$Mr_1 = (1 + \alpha) Mr_2$$

$$\frac{Mr_1}{Mr_2} = 1 + \alpha$$

$$\alpha = \frac{Mr_1 - 1}{Mr_2}$$

But $Mr = 2 \times VD$

Where VD = Vapour density

$$\text{Then vapour density of } \text{PCl}_5 = \frac{Mr}{2} = \frac{208.5}{2} = 104.25$$

From

$$\alpha = \frac{VD_1}{VD_2} - 1$$

$$\alpha + 1 = \frac{VD_1}{VD_2}$$

$$\text{But } \alpha = 0.20$$

Then

$$0.2 + 1 = \frac{104.25}{VD_2}$$

$$1.2 = \frac{104.25}{1.2}$$

$$VD_2 = 86.88$$

Qn. 77

The vapour density of iodine at atmospheric pressure and 1250°C is 87. Calculate the percentage dissociation of iodine, I_2 , into atoms in these conditions ($\text{I} = 127$)

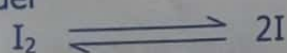
Solution

From,

$$VD_1 = \frac{254}{2} = 127$$

$$VD_2 = 87$$

Consider



From

$$\alpha = \frac{VD_1 - 1}{VD_2}$$

$$\alpha = \frac{127 - 1}{87}$$

$$\alpha = 0.46$$

That is, the iodine is 46% dissociated

DETERMINATION OF MOLECULAR MASSES OF GASES AND VOLATILE LIQUIDS

- In the 19th century, several methods of R.m.m determination were developed which all used the gas laws discussed.

- At s.t.p the molar volume of all gases is 22.4dm^3 in good approximation. Since the density is mass per unit volume, the density of gases at constant temperature and pressure is proportional to their molar mass (Graham's law)

Then the molecular masses can be calculated by one of the following methods.

- (i) Direct weighing (Regnault's method)
- (ii) Dumas method
- (iii) Victor Meyer method

(i) DIRECT WEIGHING (Regnault's method)

Recall ideal gas equation

$$PV = nRT$$

$$\text{But } n = \frac{m}{M_r}$$

$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{mRT}{PV}$$

- In this case the container of a known volume V is filled with the gas whose pressure and temperature is recorded.
- The container is then accurately weighed. Then the container is evaluated and reweighed in order to obtain the mass m of the gas. With the values obtained, the molar mass of the gas can be calculated.
- In order to minimize experimental errors, the container must be large (since only a large volume of gas has a mass which can be weighed at high accuracy, and the gas must be very pure.

(ii) DUMAS METHOD

- The Dumas method is one of the simplest ways to measure the molecular weight of a substance. In this method we have to confine a sample of gas in a container of known volume, making sure when we do this that the sample is exactly at atmospheric pressure.
- The temperature and the mass of the sample have to be measured, along with

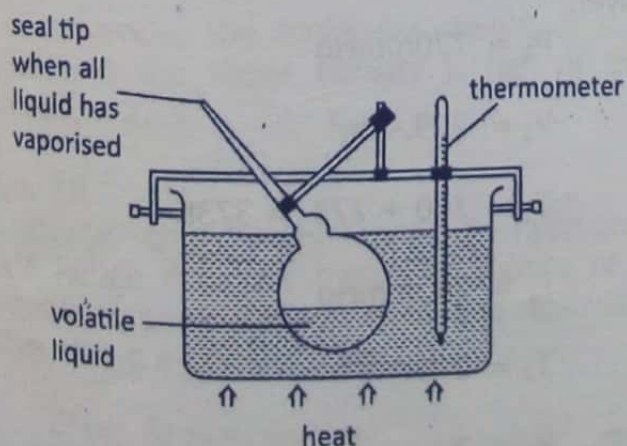
atmospheric pressure. Because liquids are much easier to handle than gases, a volatile liquid is usually used as the source of the gas.

In the classic experiment, a round thin walled glass bulb with a long, thin bent neck is weighed full of air (m_1). A small amount of volatile liquid is introduced into the bulb through a tinny opening at the end of bulbs neck so as to fill it.

The bulb is then heated in a boiling water bath to vaporize the liquid at a temperature at least 20°C above the boiling point of the liquid.

The volume of vapor formed at 100°C (temperature of boiling water) and atmospheric pressure is greater than the volume of the bulb. The vapor first pushes all of the air out of the bulb and then begins to rush out of the opening until the pressure inside the bulb equals the pressure outside (atmospheric)

With careful observation, the vapor can be seen exiting the bulb. (It looks like a jet engine exhaust or a swirling cloud.



When all the liquid is vaporized and no more vapor is seen leaving the bulb, the bulb contains a sample of vapor at atmospheric pressure and 100°C with a volume exactly equal to the volume of the bulb. The opening in the neck of the bulb is quickly sealed with flame.

It is important that the bulb be sealed at

exactly the moment that vapor stops escaping from the bulb. (sealing before vapor stops escaping will result too much vapor remains in the bulb. Molar mass calculated will be too high. Waiting too long to seal will result to low molar mass).

- The sealed bulb is cooled, dried and reweighed (m_2). The volume of the bulb must now be determined. The vapor inside has condensed, and the space above the liquid in the bulb is a near vacuum.
- Now the neck of the cooled bulb is broken under water, the water rushes into the bulb, filling it completely. The combined mass of the bulb full of water and of the glass fragments broken off is determined (m_3).
- The volume of the bulb can be determined from the mass of water it contains.
- If density of water is 1gcm^{-3} , then volume of the bulb is given by

$$\text{Volume (V)} = \frac{m_3 - m_1}{1\text{gcm}^{-3}}$$

- The mass of the bulb is m_1 since the upthrust (the mass of air displaced by the closed bulb) balances the mass of air contained in the bulb.

$$\text{Up thrust} = \rho_{\text{air}} \times V$$

Hence mass of the vapor which filled the bulb is $m_2 - m_1 + \text{upthrust}$. (at the recorded pressure and temperature).

- The volume V is then reduced to s.t.p using the general gas equation and the mass of 22.4dm^3 of the vapour at s.t.p is calculated. This gives the molar mass.

Qn 78.

Calculate the vapor density and molecular weight of a volatile liquid X, from the following data.

- Weight of Dumas bulb full of air to

$$10^{\circ}\text{C and } 770\text{mmHg} = 25.7\text{g}$$

- Weight of bulb sealed full of vapor of X at 100°C and $770\text{ mmHg} = 25.759\text{g}$
- Weight of bulb full of water = 265.1g

Given

1 liter of hydrogen at S.T.P weighed 0.09g

1 liter of air at s.t.p weighed 1.293g

Solution

1st Case:

Find the capacity of the bulb from the weight of water contained.

i.e.

$$\text{Mass of water in the bulb} = (265.1 - 25.7)\text{g} = 239.4\text{g}$$

$$\text{That is, capacity of the bulb} = 239.4\text{cm}^3$$

2nd Case:

Convert the volume of the contained air at s.t.p, find its weight and hence, the weight of the evacuated bulb.

Volume of air in the bulb at s.t.p

From,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Where,

$$P_1 = 770\text{mmHg}$$

$$V_1 = 239.4\text{cm}^3$$

$$T_1 = 283\text{K}$$

$$P_2 = 760\text{mmHg}$$

$$V_2 = ?$$

$$T_2 = 273\text{K}$$

Then

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{770 \times 239.4 \times 273}{283 \times 760} = 234\text{cm}^3$$

3rd case: Find the mass of air in the bulb at s.t.p its density is 1.293g/L

$$\begin{array}{ccc} \text{From } 1.293\text{g} & \longrightarrow & 1000\text{cm}^3 \\ x & \longleftarrow & 234\text{cm}^3 \end{array}$$

$$x = 0.303\text{g}$$

Thus the weight of air in the bulb is 0.303g

4th case:

Find the weight of evacuated bulb

$$\text{Wt of empty bulb} = \text{wt of bulb full of air} - \text{wt of air}$$

$$\begin{aligned} \text{Wt of evacuated bulb} &= 25.7\text{g} - 0.303\text{g} \\ &= 25.397\text{g} \end{aligned}$$

5th case:

Find the weight of vapour sealed into the bulb

i.e.

$$\begin{aligned} \text{Wt of vapour in the bulb} &= 25.759 - 25.397\text{g} \\ &= 0.362\text{g} \end{aligned}$$

6th case:

Convert volume of vapour to s.t.p

Given,

$$P_1 = 770\text{mmHg}$$

$$V_1 = 239.4\text{cm}^3$$

$$T_1 = 100 + 273 = 373\text{K}$$

$$P_2 = 760\text{mmHg}$$

$$T_2 = 273$$

$$V_2 = ?$$

From

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{770 \times 239.4 \times 273}{760 \times 373}$$

$$V_2 = 177.5\text{cm}^3$$

7th case:

Calculate the vapor density and molecular weight of X.

i.e. Wt of volume of hydrogen equals to volume of vapor at s.t.p

i.e. If $0.09g \longrightarrow 1000cm^3$
 $x \longleftarrow 177.5cm^3$

$$x = 0.016g.$$

Vapor density of x

$$= \frac{\text{weight of } x}{\text{weight of } H_2}$$

$$= \frac{0.363g}{0.016g} = 22.6$$

Then Molecular weight of x = $22.6 \times 2 = 45.2 \text{ gmol}^{-1}$.

Note:

If the use of G.M.V = 22.4litres at s.t.p is referred, the last few lines of the calculation will run.

i.e.

$177.5cm^3 \longrightarrow 0.362g$
 $22400cm^3 \longleftarrow xg$

$$x = 45.7g \text{ (per one mole)}$$

Consequently, the molecular weight of x is 45.7 and the vapor density is half of this value i.e. 22.9

Qn. 79

Calculate the density relative to hydrogen, and hence find the molecular weight of a volatile organic liquid, from the following data, using a Dumas' bulb.

- Wt. of bulb and air..... 30.78g
- Wt of bulb and vapor after sealing 31.03g
- Wt of bulb full of water (and piece broken off) = 209g
- Temperature of laboratory 20°C
- Temperature of bath at moment of sealing 73°C.

- Pressure..... 755mmHg.

Assume,

1 liter of dry air at s.t.p weighs 1.2939g

1 liter of dry hydrogen at s.t.p weighs 0.09g

Solution

1st case:

Find the capacity of the bulb from the weight of water contained.

i.e.

$$\text{Wt. of water in the bulb} = (209 - 30.78)g \\ = 178.22g$$

$$\text{That is, capacity of bulb} = 178.22cm^3$$

2nd case:

Convert the volume of the contained air to s.t.p, find its weight and hence the weight of evacuated bulb

Then,

Volume of air in the bulb at s.t.p

$$P_1 = 755mmHg$$

$$V_1 = 178.22cm^3$$

$$T_1 = 293K$$

$$P_2 = 760mmHg$$

$$V_2 = ?$$

$$T_2 = 273$$

Then,

From,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{755 \times 178.22 \times 273}{293 \times 760}$$

$$V_2 = 165cm^3$$

Weight of air in the bulb

$$\begin{array}{ccc} \text{From } 1.293\text{g} & \longrightarrow & 1000\text{cm}^3 \\ x & \longleftarrow & 165\text{cm}^3 \end{array}$$

$$x = 0.213\text{g}$$

Then weight of air in 165cm^3 is 0.213g .

$$\begin{aligned} \text{Weight of evaluated bulb} &= 30.78 - 0.213 \\ &= 30.5\text{g} \end{aligned}$$

3rd case: Find the weight of vapor sealed into the tube

i.e.

$$\begin{aligned} \text{Wt of vapor in the bulb} &= 31.03 - 30.57 \\ &= 0.46\text{g} \end{aligned}$$

4th case:

Convert the volume of vapor to s.t.p

Given

$$V_1 = 178.22\text{cm}^3$$

$$P_1 = 755\text{mmHg}$$

$$T_1 = 346\text{K}$$

$$P_2 = 760\text{mmHg}$$

$$V_2 = ?$$

$$T_2 = 273\text{K}$$

From

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{755 \times 178.22 \times 273}{760 \times 346}$$

$$V_2 = 139.69\text{cm}^3$$

5th case:

Calculate the vapor density and hence Mr.

$$\begin{array}{ccc} \text{Then If,} & 0.09 \text{ of H}_2 \longrightarrow & 1000\text{cm}^3 \\ & x \text{ g of H}_2 \longleftarrow & 139.69\text{cm}^3 \end{array}$$

$$x = \frac{0.09 \times 139.69}{1000}$$

$$x = 0.0126$$

$$\text{Then VD} = \frac{0.46}{0.0126} = 36.6$$

Then the vapor density of volatile organic liquid is 36.6 and molar mass is 73.2g mol^{-1}

Qn 80:

Calculate the molecular weight of carbon dioxide from the following data

- Wt of evacuated globe..... 27.3g
- Wt of globe full of carbon dioxide at 17°C and 758mmHg is 28.4g
- Wt of globe full of water is 621.4g

Solution

1st case:

Find the capacity of the globe from the weight of a water it contains

Thus ,

$$\begin{aligned} \text{Wt of water} &= (621.4 - 27.3)\text{g} \\ &= 594.1\text{g} \end{aligned}$$

Thus, capacity of globe

$$= 594.1\text{cm}^3$$

2nd case:

Find the weight of carbon dioxide contained in the globe.

$$\begin{aligned} \text{Wt of CO}_2 &= (28.4 - 27.3)\text{g} \\ &= 1.1\text{g} \end{aligned}$$

3rd case: Convert the volume of CO_2 to s.t.p

Given,

$$P_1 = 758\text{ mmHg}$$

$$V_1 = 594.1\text{cm}^3$$

$$T_1 = 290\text{K}$$

$$P_2 = 760\text{mmHg}$$

$$T_2 = 273\text{K}$$

$$V_2 = ?$$

From,

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{758 \times 594.1 \times 273}{760 \times 290}$$

$$V_2 = 557.8 \text{ cm}^3$$

then from,

$$\begin{array}{lcl} 1.1 \text{ g of CO}_2 & \longrightarrow & 557.8 \text{ cm}^3 \\ x \text{ g of CO}_2 & \longleftarrow & 22400 \text{ cm}^3 \end{array}$$

$$x = \frac{1.1 \times 22400}{557.8} = 44.17 \text{ g/mol.}$$

Then the molecular weight of carbon dioxide is 44.17 g/mol

Qn 81

Calculate the molecular weight of a gas x from the following data alone:-

- Wt. of evacuated globe..... 11.27g
- Wt. of globe filled with hydrogen...11.63g
- Wt. of globe filled with gas x.....19.18g

Temperature and pressure were constant throughout the experiment

Solution

1st case:

Find the weight of hydrogen contained in globe

i.e.

$$\begin{aligned} \text{Wt. of H}_2 &= (11.63 - 11.27) \text{ g} \\ &= 0.36 \text{ g} \end{aligned}$$

2nd case:

Find the weight of gas x contained in globe

i.e.

$$\begin{aligned} \text{Wt. of gas x} &= (19.18 \text{ g} - 11.27 \text{ g}) \\ &= 7.91 \text{ g} \end{aligned}$$

3rd case:

Find the vapor density of the gas x from the wt. of gas x and wt. of H₂

i.e.

$$\text{VD} = \frac{\text{Wt. of x}}{\text{Wt. of H}_2} = \frac{7.91}{0.36} = 21.97$$

Then the molar mass equal to $(2 \times \text{VD}) \approx 2 \times 21.97 = 43.94 \text{ g mol}^{-1}$

Qn 82:

Find the density relative to hydrogen and the molecular weight of chloroform from the following Dumas experiment.

- Wt. of bulb filled with air at 17°C and 755 mmHg is 25.23g
- Wt. of bulb filled with vapor at 80°C and 755 mmHg is 25.697g
- Wt. of bulb filled with water is 184.73g

Given

1 liter of dry air at s.t.p weighs 1.293g

1 liter of dry hydrogen at s.t.p weighs 0.09g

Solution

1st case:

Find the capacity of the bulb from the weight of water contained.

i.e.

$$\begin{aligned} \text{Wt. of water in the bulb} &= (184.73 - 25.23) \text{ g} \\ &= 159.5 \text{ g} \end{aligned}$$

That is, capacity of bulb

$$= 159.5 \text{ cm}^3$$

2nd case:

Convert the volume of contained air to s.t.p find its weight, and hence, the weight of evacuated bulb.

i.e.

Volume of air in the bulb at s.t.p

$$P_1 = 755 \text{ mmHg}$$

$$V_1 = 159.5 \text{ cm}^3$$

$$T_1 = 290 \text{ K}$$

$$P_2 = 760 \text{ mmHg}$$

$$T_2 = 273 \text{ K}$$

$$V_2 = ?$$

From,

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{755 \times 159.5 \times 273}{760 \times 290}$$

$$V_2 = 149.16 \text{ cm}^3$$

Weight of air in the bulb

From,

$$\begin{array}{l} 1.293 \text{ g} \longrightarrow 1000 \text{ cm}^3 \\ x \text{ g} \longleftarrow 149.16 \text{ cm}^3 \end{array}$$

$$x \text{ g} = 0.193 \text{ g}$$

Then wt. of air in the bulb is 0.193g

Weight of evacuated bulb

$$= 25.23 - 0.193 \text{ g}$$

$$= 25.037 \text{ g}$$

3rd case:

Find the weight of vapor sealed into the bulb

i.e.

$$\begin{aligned} \text{Wt of vapor in bulb} &= 25.697 - 25.037 \text{ g} \\ &= 0.66 \text{ g} \end{aligned}$$

4th case:

Convert the volume of vapour to s.t.p

i.e.

Volume of vapour at s.t.p

$$P_1 = 755 \text{ mmHg}$$

$$V_1 = 159.5 \text{ cm}^3$$

$$T_1 = 353 \text{ K}$$

$$P_2 = 760$$

$$T_2 = 273$$

$$V_2 = ?$$

From,

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{755 \times 159.5 \times 273}{760 \times 353}$$

$$V_2 = 122.54 \text{ cm}^3$$

5th case:

- Calculate the vapor density and molecular wt of chloroform

- Notice that wt. of volume of hydrogen equal to volume of vapor at S.T.P

i.e.

$$\begin{array}{l} 0.09 \text{ g of H}_2 \longrightarrow 1000 \text{ cm}^3 \\ x \text{ g of H}_2 \longrightarrow 122.54 \text{ cm}^3 \end{array}$$

Then

$$x = \frac{0.09 \times 122.54}{1000} = 0.011 \text{ g}$$

Then

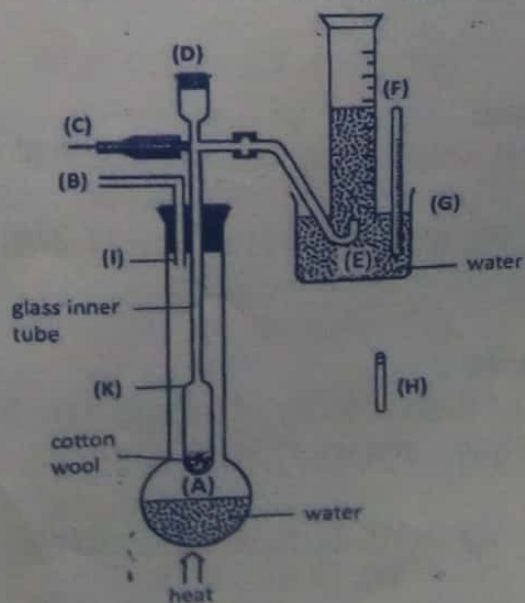
$$\text{VD} = \frac{\text{Wt. of vapour}}{\text{Wt. of H}_2} = \frac{0.66}{0.011} = 60$$

- Then the density of chloroform relative to hydrogen is 60 and the molar mass is twice this value i.e. 120 gmol^{-1}

VICTOR MEYER'S METHOD

- This method is used for volatile liquids like CS_2 , ethoxy ethane (ether), ethanol etc.

- A small stoppered tube (H) (Figure below) is weighed first empty (m_1) and then containing the volatile liquid (m_2)



- First the graduated cylinder, F, is omitted and the water below (A) heated to boiling. Air will escape at (E) until steam escapes at (B) and the air inside the inner

tube (K) has reached a steady state (about a 100°C between (A) and (I). Now the cylinder (F) full of water, is placed on top of (E)

Now the small weighed tube (H) containing the volatile liquid is inserted at (D) but held with the glass rod (C) until the stopper (D) is again placed air-tight. Then (C) is pulled aside so that (H) falls to (A). Then cotton-wool prevents breakage

Due to temperature of about 100°C at (A), the sample will vaporize and push the stopper off the bottle (H). Hence air is expelled at E and collected by F.

When no more air is expelled (F) is moved from (E) and lowered into the water until the levels in (F) and (G) are equal. Now the air inside (F) is at atmospheric and its volume is recorded. Also the temperature of the water in (G) and the atmospheric pressure are written down. Furthermore, the vapor pressure of water at the temperature of (G) is needed.

The volatile liquid should not have a B.P of above 80°C so that the boiling water can easily vaporize it. Otherwise, a higher boiling point heating liquid eg (phenyl amine b.p 184°C) must be used instead of water.

The vapor of the volatile liquid will not reach much above (K) since the narrow tube allows only slow diffusion. If the vapor would reach I, it would condense and the experiment would be useless.

Thus only air is expelled at (E) representing the volume of the vapor if it could exist under room conditions. Of course, since the air is collected over water, its partial pressure must be found according to Dalton's law.

Qn 83.

0.143g of volatile liquid, when vaporized in a

V. Meyer apparatus, displaced 30.4cm^3 of air at 17°C and 745mmHg . Calculate the vapor density and molecular weight of the liquid (The vapor pressure of water at 17°C is 15mm).

Solution

Method 1:

Using the fact that one liter of H_2 at S.T.P weighs 0.09g .

1st case:

Find volume of air displaced at S.T.P

Given

$$V_1 = 30.4 \text{ cm}^3$$

$$P_1 = (745-15)\text{mmHg}$$

$$T_1 = 290\text{K}$$

$$P_2 = 760\text{mmHg}$$

$$T_2 = 273\text{K}$$

$$V_2 = ?$$

From,

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{730 \times 30.4 \times 273}{760 \times 290}$$

$$V_2 = 27.5\text{cm}^3$$

Then wt. of this volume of hydrogen at S.T.P

i.e.

$$\begin{array}{l} \text{If } 0.09\text{gH}_2 \longrightarrow 1000\text{cm}^3 \\ x \text{ g of H}_2 \longleftarrow 27.5\text{cm}^3 \end{array}$$

$$x = \frac{0.09 \times 27.5}{1000}$$

$$x = 0.00248\text{g}.$$

2nd case:

Find the vapour density of the liquid and molecular weight

i.e.

$$\text{VD} = \frac{\text{Weight of vapour}}{\text{Weight of H}_2} = \frac{0.143}{0.00248} = 57.7$$

Then,

$$\begin{aligned}\text{Molecular weight of the liquid} &= V.D \times 2 \\ &= 57.7 \times 2 \\ &= 115.4 \text{ g mol}^{-1}\end{aligned}$$

Alternatively (method 2)

Using the fact that the G.M.V of a gas is 22.4 litres of air at S.T.P,
i.e.

From the volume of displaced air converted to s.t.p is 27.5 cm^3 . The liquid which displaced this air is 0.143 g .

Therefore,

Weight of liquid needed to displace 22.4 litres of air at s.t.p

$$\begin{array}{lcl} \text{i.e.} & 0.143 \text{ g} & \longrightarrow 27.5 \text{ cm}^3 \\ & x \text{ g} & \longleftarrow 22400 \text{ cm}^3 \end{array}$$

$$x = \frac{0.143 \times 22400}{27.5 \text{ cm}^3}$$

$$x = 116.5 \text{ g mol}^{-1}$$

Thus, molecular weight of liquid is 116.5 and its vapour density is half this figure i.e. 58.3

Notice

The two calculations give results differing by 1%. The reason is that, if the datum, 1 liter of H_2 at S.T.P weighs 0.09 g, is used, $H \approx 1$. But if G.M.V = 22.4 liters at s.t.p is taken, $H \approx 1.008$

Qn. 84.

Find the molecular weight of a volatile liquid from the following Victor Meyer experiment.

- Wt. of small stoppered tube ... 0.672 g
- Wt. of small stoppered tube + liquid 0.783 g
- Volume of air displaced 35.8 cm^3
- Temperature 12°C
- Pressure 756 mmHg
- Vapour pressure of water vapour at 12°C is 11 mmHg

Solution

1st case:

Find the mass of volatile liquid in stoppered tube

i.e.

$$\begin{aligned}\text{Wt. of liquid} &= 0.783 - 0.672 \\ &= 0.111 \text{ g}\end{aligned}$$

2nd case:

Find the volume of air displaced at s.t.p

Given,

$$P_1 = (756 - 11) \text{ mmHg}$$

$$V_1 = 35.8 \text{ cm}^3$$

$$T_1 = 12 + 273$$

$$P_2 = 760 \text{ mmHg}$$

$$V_2 = ?$$

$$T_2 = 273$$

From

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{745 \times 35.8 \times 273}{760 \times 285}$$

$$V_2 = 33.62 \text{ cm}^3$$

3rd case:

Find weight of liquid needed to displace 22.4 L at s. t. p

i.e.

$$\begin{array}{lcl} \text{If,} & 0.111 \text{ g} & \longrightarrow 33.62 \text{ cm}^3 \\ & x \text{ g} & \longleftarrow 22400 \text{ cm}^3 \end{array}$$

$$\text{Then } x = \frac{0.111 \text{ g} \times 22400 \text{ g/mol}}{33.62}$$

$$= 73.96 \text{ g mol}^{-1}$$

Or

Find mass of hydrogen of this volume at S.T.P

i.e.

$$\begin{array}{lcl} 0.09 \text{ g H}_2 & \longrightarrow & 1000 \text{ cm}^3 \\ x & \longleftarrow & 33.62 \text{ cm}^3 \end{array}$$

$$\begin{aligned}x \text{ g of H}_2 &= \frac{0.09 \times 33.62}{1000} \\ &= 0.003026 \text{ g}\end{aligned}$$

Then

$$VD = \frac{\text{weight of volume of H}_2 \text{ liquid}}{\text{Weight of equal volume of H}_2}$$

$$VD = \frac{0.111}{03.026 \times 10^{-3}} = 36.68$$

$$\begin{aligned} \text{Then molecular weight} &= 36.68 \times 2 \\ &= 73.4 \text{ g mol}^{-1} \end{aligned}$$

Qn 85:

0.119g of a volatile liquid when vaporized in a victor Meyer's apparatus displaced 25.4cm³ of air at 17°C and 745 mmHg. Calculate the molecular weight of the liquid. Vapour pressure of water at 17°C is 15mmHg.

Solution

1st case

Find the volume of air displaced at S.T.P

Given,

$$\begin{aligned} V_1 &= 25.4 \text{ cm}^3 \\ P_1 &= 730 \text{ mmHg} \\ T_1 &= 290 \text{ K} \\ V_2 &= ? \\ P_2 &= 760 \text{ mmHg} \\ T_2 &= 273 \text{ K} \end{aligned}$$

From

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{730 \times 25.4 \times 273}{760 \times 290}$$

$$V_2 = 22.97 \text{ cm}^3$$

2nd case:

Find the weight of liquid needed to displace 22.4L at s.t.p

$$\begin{array}{lcl} \text{i.e.} & \text{if} & \\ 0.119\text{g} & \longrightarrow & 22.97 \text{ cm}^3 \\ \text{xg} & \longleftarrow & 22400 \text{ cm}^3 \end{array}$$

$$x = \frac{0.119 \times 22400}{22.97}$$

$$x = 116 \text{ g mol}^{-1}$$

Then the molecular weight of liquid is 116 g mol⁻¹

Alternatively

Then weight of hydrogen at this volume of 22.97 at s.t.p is ,

$$\frac{0.09 \times 22.97}{1000} = 2.0673 \times 10^{-3} \text{ g}$$

Then ,

$$\text{Vapour density} = \frac{\text{weight of volatile liquid}}{\text{weight of equal value of H}_2}$$

$$VD = \frac{0.119 \text{ g}}{2.0673 \times 10^{-3}}$$

$$VD = 57.56$$

Then molecular weight is twice this value i.e.
57.56 x 2 = 115 g mol⁻¹

Qn 86.

Calculate the molecular weight of a volatile liquid from the following results of a determination by V. Meyer's method

- Weight of small stoppered tube is 1.26g
- Weight of small stoppered tube + liquid 1.50g
- Volume of air displaced (over water) 30.9cm³
- Temperature of air..... 17°C
- Height of barometer..... 75cm
- Vapour pressure of water at 17°C 15mmHg

Solution

1st case:

Find the mass of the liquid in the stopper tube

i.e.

$$\begin{aligned} \text{wt. of liquid} &= 1.506 \text{ g} - 1.26 \text{ g} \\ &= 0.246 \text{ g} \end{aligned}$$

2nd case:

Find the volume of air displaced at s.t.p

Given

$$V_1 = 30.9\text{cm}^3$$

$$P_1 = 75\text{cm} = (750\text{mm} - 15\text{mm})\text{Hg}$$

$$T_1 = 290\text{K}$$

$$P_2 = 760\text{mmHg}$$

$$T_2 = 273\text{K}$$

$$V_2 = ?$$

From

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{735 \times 30.9 \times 273}{290 \times 760}$$

$$V_2 = 28.13\text{cm}^3$$

3rd case:

Find the mass of liquid needed to displace 22.4L at s.t.p. The value obtained equals to molar mass

If,

$$\begin{array}{lcl}
 0.246\text{g of liquid} & \longrightarrow & 28.13\text{cm}^3 \\
 x\text{ g of liquid} & \longleftarrow & 22400\text{cm}^3
 \end{array}$$

$$x = \frac{0.246 \times 22400}{28.13} \text{ g mol}^{-1}$$

$$x = 195.9\text{g mol}^{-1}$$

Qn 87:

In a Victor Meyer determination of the vapour density of a volatile liquid, 0.078g of the liquid displaced 23.5cm³ of air measured over water at 14°C and 762mmHg. If the vapour pressure of water at 14°C is 13mmHg. Calculate the molecular weight of the liquid.

Solution**1st case:**

Find the volume of air displaced at s.t.p

Given,

$$V_1 = 23.5\text{cm}^3$$

$$P_1 = 762 - 13 = 749\text{mmHg}$$

$$T_1 = 287\text{K}$$

$$V_2 = ?$$

$$P_2 = 760\text{mmHg}$$

$$T_2 = 273\text{K}$$

From,

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$V_2 = \frac{749 \times 23.5 \times 273}{760 \times 287}$$

$$V_2 = 22.03\text{cm}^3$$

2nd case:

Find the weight of liquid needed to displace 22.4L at s.t.p;

i.e. If,

$$\begin{array}{lcl}
 0.078\text{g} & \longrightarrow & 22.03\text{cm}^3 \\
 x\text{ g} & \longleftarrow & 22400\text{cm}^3
 \end{array}$$

$$x = \frac{0.078 \times 22400}{22.03} \text{ g mol}^{-1} = 79.3\text{g mol}^{-1}$$

Hence the molecular weight of the liquid is 79.3g mol⁻¹.

2. LIQUID STATE (SOLUTIONS)

What is a solution?

Is a homogeneous mixture of two or more substances (components). By homogeneous mixture we mean that its composition and properties are uniform throughout the mixture.

Generally the component that is present in the largest quantity is known as solvent. One or more components present in the solution other than solvent are called solutes.

Types of solutions

Below are the common types of solutions.

- Liquid - Liquid solutions e.g. Vodka in water.
- Solid - Liquid solutions e.g. Sugar solutions
- Gas - Liquid solutions e.g. Carbonated water (soda).

Note

Chemists also characterize solution by their capacity to dissolve a solute.

A saturated solution, contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An unsaturated solution, contains less solute than it has the capacity to dissolve.

A supersaturated solution, contains more solute than is present in a saturated solution.

A MOLECULAR VIEW OF THE SOLUTION PROCESS

The intermolecular attractions that hold molecules together in liquids and solids also play a central role in the formation of solutions.

When one substance (the solute) dissolves in another (solvent), particles of the solute disperse throughout the solvent.

- The solute particles occupy positions that are normally taken by solvent molecules. The ease with which a solute particle replace a solvent molecule depends on the relative strengths of three types of attractions:

- Solvent - solvent interaction
- Solute - solute interaction
- Solvent - solute interaction

- For simplicity, we can imagine the solution process taking place in three distinct steps.

1st step

Separation of solvent molecules

2nd step.

Entails the separation of solute molecules.

- These steps require energy input to break attractive intermolecular forces; therefore, they are endothermic

3rd step

- The solvent and solute molecules mix. This process can be exothermic or endothermic. The heat of solution ΔH_{soln} is given by

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

-If the solute-solvent is stronger than the solvent-solvent attraction and solute-solute attraction, the solution process is favourable, or exothermic ($\Delta H_{\text{soln}} < 0$)

If the solute-solvent interaction is weaker than the solvent-solvent. Solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H_{\text{soln}} > 0$).

SOLUTIONS PREPARED BY MIXING TWO LIQUIDS (BINARY SOLUTIONS).

- Liquid-liquid solutions can be classified into two types: -
 - i) Ideal solutions
 - ii) Non ideal solutions.
- Classifications of these solutions into ideal

and non ideal is based on comparing the inter-molecular forces (adhesive force) existing in the solution and inter-molecular forces (cohesive force) existing in pure solvents.

i) IDEAL SOLUTIONS

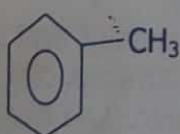
What is an ideal solution?

- Is a solution whose intermolecular forces existing in solution are equal to inter-molecular forces existing in pure solvents and such solution obeys the Raoult's law over the entire range of concentration.
- This means that solvent-solvent, solute - solute and solute - solvent attractions are all the same. Or solvent A-solvent A, solvent B-solvent B and solvent A-solvent B attractions are the same.
- For example, a solution of the non polar benzene in the non polar toluene (methylbenzene) is very close to an ideal solution.

i.e.



Benzene



Toluene

PROPERTIES OF IDEAL SOLUTIONS

Ideal solutions have the following properties/characteristics

- Ideal solution must obey the Raoult's law over a wide range of concentration.
- There is neither contraction nor expansion of volume of the resulting mixture solution. For example if 20cm^3 of solvent A is mixed with 30cm^3 of solvent B, the volume of ideal solution would be 50cm^3 .
- The heat of mixing of pure components to form solution is zero, this means that heat is neither absorbed nor released in forming ideal solution.
- Boiling point of the solution lies in between the boiling point of the pure sol-

vents. For example if solvent A boils at 20°C and solvent B boils at 40°C , then boiling point of the solution will lie in between 20°C to 40°C .

- When distilled an ideal solutions do not form Azeotropic mixture.

RAOULTS LAW AND IDEAL SOLUTION.

- Raoult's law is concerned with determination of partial (equilibrium) vapour pressure exerted by the components above an ideal solution.
- Raoult's law states that. **"The equilibrium vapour pressure of a volatile component over an ideal solution is given by the product of its mole fraction in solution and the saturated vapour pressure of the pure substance at the same temperature as the solution"**.

Note.

Saturated vapour pressure:- Is the maximum vapour pressure that can developed by a liquid.

Mole fraction:- Is the ratio of number of moles of a certain component to the total number of moles of all components in the solution. (it is denoted by χ).

For example, for component A.

$$\chi_A = \frac{n_A}{n_T}$$

Where,

n_A = Number of moles of A.

n_T = Total number of moles

- Clearly the sum of all mole fractions must be unity. For example in a two components solution A and B.

$$\chi_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad \chi_B = \frac{n_B}{n_B + n_A}$$

Hence $\chi_A + \chi_B = 1$.

- If P_A is the equilibrium (partial) vapour pressure of component A in solution, χ_A is

the mole fraction of that component in solution and P_A is the saturated vapour pressure of pure component, then Raoult's law can be expressed algebraically as,

$$P'_A = \chi_A P_A \dots\dots\dots (i)$$

Also for component B

$$P'_B = \chi_B P_B \dots\dots\dots (ii)$$

But in a mixture of A and B

$$n_T = n_A + n_B$$

Then,

$$P'_A = \frac{n_A}{n_A + n_B} \times P_A$$

Also

$$P'_B = \frac{n_B}{n_B + n_A} \times P_B$$

Where:-

n_A = number of moles of A in solution

n_B = number of moles of B in solution

$\chi_A = \frac{n_A}{n_A + n_B}$ = Mole fraction of A in the solution

$\chi_B = \frac{n_B}{n_A + n_B}$ = Mole fraction of B in the solution.

P'_A = Partial vapour pressure of component A, exerted above ideal solution

P'_B = Partial vapour pressure of component B exerted above ideal solution.

P_A = Vapour pressure of pure A.

P_B = Vapour pressure of pure B.

Note.

- Partial vapour pressure of the compo-

ponents are assumed to be gases hence the total vapour pressure are calculated just according to Dalton's law of partial pressure.

i.e. $P_T = P'_A + P'_B$

Or

$$P_T = \chi_A \cdot P_A + \chi_B \cdot P_B$$

- Composition of the vapour (mole fraction in vapour) above an ideal solution is obtained by taking ratio of partial vapour pressure of the component to the total vapour pressure.

i.e.

$$\text{Composition of vapour} = \frac{\text{Partial vapour pressure}}{\text{Total vapour pressure}}$$

Or

$$C_A = \frac{P'_A}{P_T}$$

Where

C_A = Composition (mole fraction) of A in Vapour

P_T = Vapour pressure of the solution (Total vapour pressure).

VAPOUR PRESSURE –MOLE FRACTION PHASE DIAGRAM FOR IDEAL SOLUTION.

- Is the graph which shows the relationship between the mole fraction of the components present in the solution, partial vapour pressure of the component and total vapour pressure.

Note:

- Any liquid is involved in the equilibrium,

$$X_{(l)} \rightleftharpoons X_{(g)}$$

- This also happens to a lesser degree on the surface of a solid. This is called phase equilibrium because the only thing changing is the phase that the substance is in.

this lead to the conclusion that there is a vapour present above any liquid or solid. This can be observed with a bottle of ethanol the smell of the alcohol is noticeable when the bottle is opened.

- **The vapour pressure** of a liquid is the pressure exerted by the vapour above the liquid. This is affected by volatility of the liquid in question. (a more volatile liquid will have a higher vapour pressure) and the temperature (the vapour pressure increases with temperature)
- Boiling point can be related to vapour pressure i.e. A lower boiling point means that the liquid is more volatile and therefore has a great vapour pressure.
- Suppose you have an ideal mixture of two liquids A and B. Now according to Raoult's law, "The partial vapour pressure of A (for example) at a particular temperature directly proportional to its mole fraction.

i.e.

$$P'_A \propto \chi_A$$

Or

$$P'_A = P_A \cdot \chi_A$$

This expression is in the form of $y = mx$.

Where,

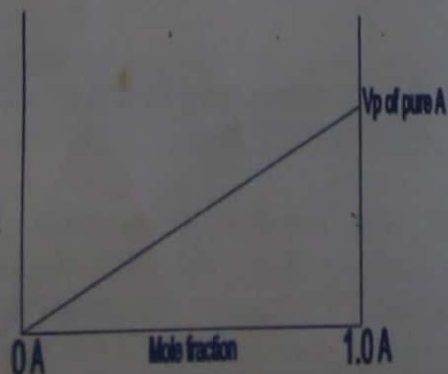
$y = P'_A$ (vapour pressure of A above mixture)

$x = \chi_A$ (mole fraction)

$m = P_A$ (slope)

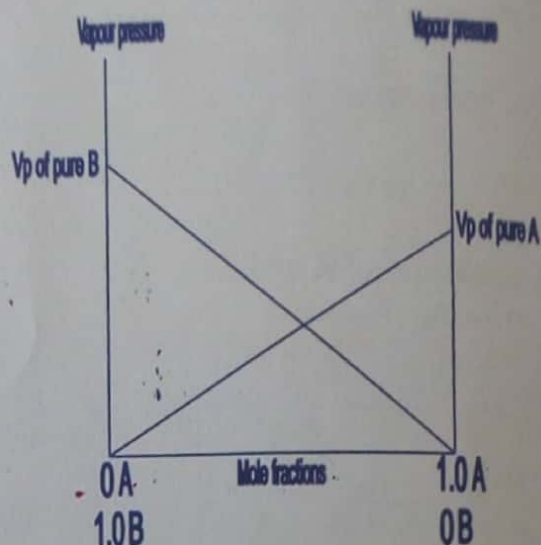
- If you plot the graph of the partial vapour pressure of A against its mole fraction, you will get a straight line.

i.e.

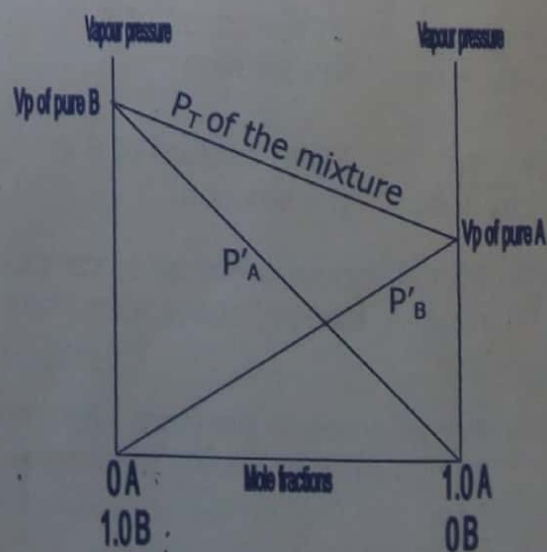


Now we'll do the same thing for B-except that we will plot it on the same set of axes. The mole fraction of B falls as A increases so the line will slope down rather than up. As the mole fraction of B falls, its vapour pressure will fall at the same rate.

i.e.



- Notice that the vapour pressure of B is higher than that of pure A. This means that molecules must break away more easily from the surface of B than of A, B is more volatile than A.
- To get total vapour pressure of the mixture, you need to add values for A and B together at each composition. The net effect of that is to give you a straight line as shown in the next diagram.



BOILING TEMPERATURE-COMPOSITION CURVE FOR IDEAL SOLUTIONS.

- Is the graph which shows the boiling point of the solution, composition of the vapour and distillate. It is sometimes

known as boiling temperature mole fraction phase diagram.

Note:

- If a liquid has a high vapour pressure at a particular temperature, it means that its molecules are escaping easily from the surface.
- If at the same temperature a second liquid has a low vapour pressure, it means that its moles aren't escaping so easily.

Qn.

What does this imply about the boiling of the two liquids?

Ans.

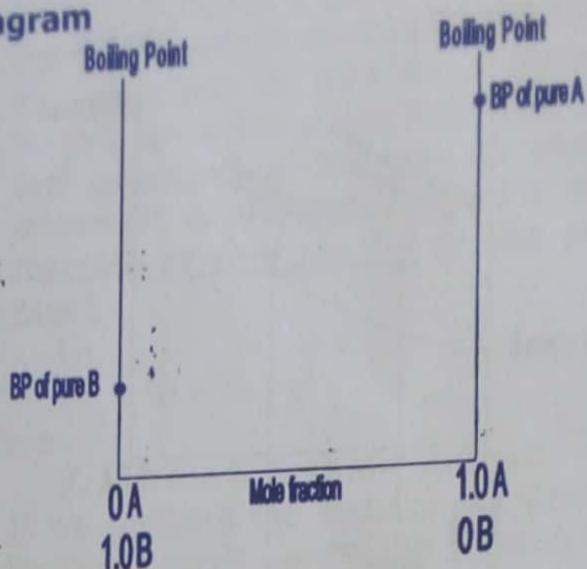
There are two ways of looking at this, choose one:-

- If the molecules are escaped easily from the surface, it must mean that the inter-molecular forces are relatively weak. This means that you won't have to supply so much heat to break them completely and boil the liquid.
- The liquid with the higher vapour pressure at a particular temperature is the one with the lower boiling points

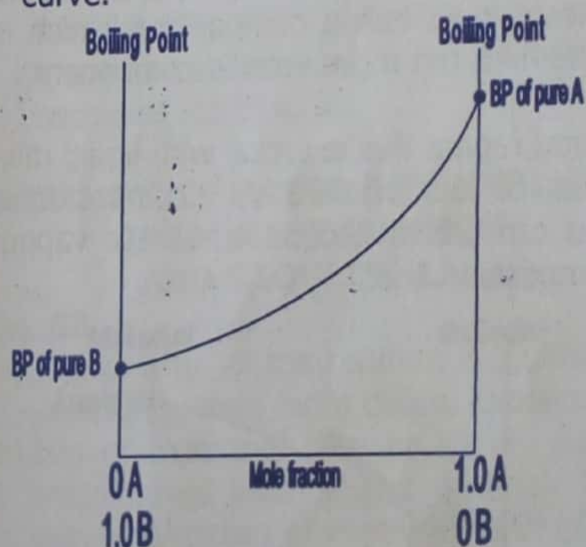
OR

- Liquid boil when their vapour pressure becomes equal to the external pressure. If a liquid has a high vapour pressure at some temperature, you won't have to increase the temperature very much until the vapour pressure reaches the external pressure. On the other hand if the vapour pressure is low, you will have to heat it up a lot more to reach the external pressure.
- Consider an ideal solution (mixture) prepared from solvent A and B in which B has high vapour pressure than A.
- High vapour pressure implies low boiling point

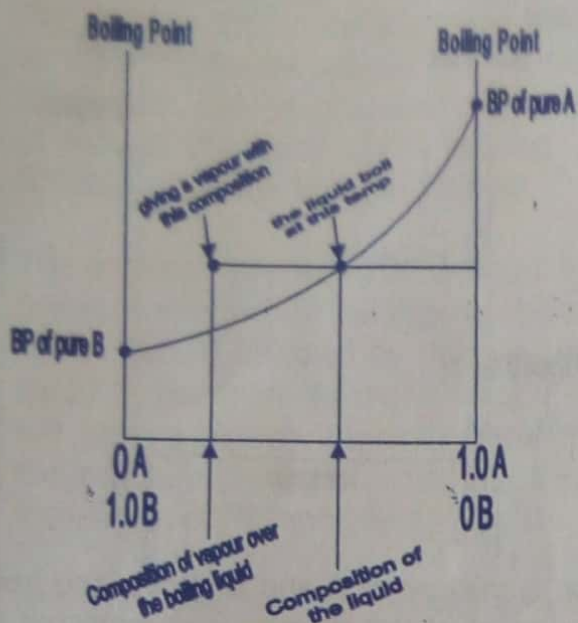
Diagram



- For a mixture of A and B above, the boiling point of the mixture was expected to be a straight line joining the two points. But it is not so, in fact, it turns to be a curve.

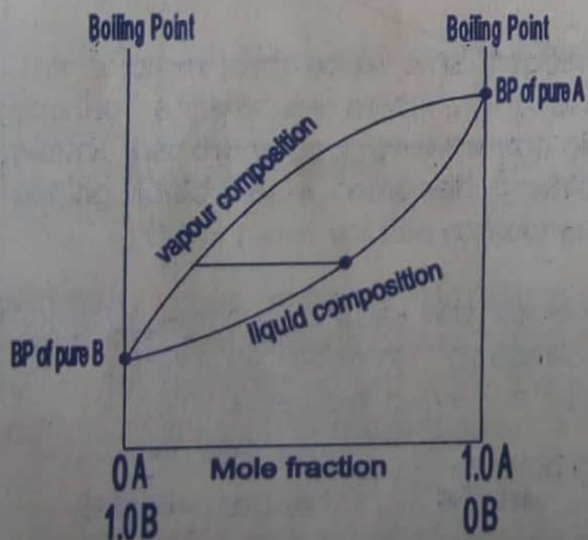


- To make this diagram really useful, we are going to add another line. This second line will show the composition of the vapour over the top of any particular boiling point.
- If you boil a liquid mixture, you would expect to find that the more volatile substance escapes to form vapour more easily than the less volatile one.
- This means that, in our case above, you would expect to find higher proportion of B (more volatile) in the vapour than in the liquid. You can discover this composition by condensing the vapour and analyzing it.



- The diagram just shows what happens if you boil a particular mixture of A and B. Notice that the vapour over the top of the boiling liquid has a composition which is richer in B the more volatile component.

- If you repeat this exercise with liquid mixtures of lots of different compositions, you can plot a second curve - a vapour composition line.



We call the above line as **tie line** and it intersect the upper curve at the composition of the vapour in equilibrium with the liquid at the same temperature. The region between the two curves is a two phase region. In this region, two phases i.e. Liquid and gas (vapour) are in equilibrium with each other.

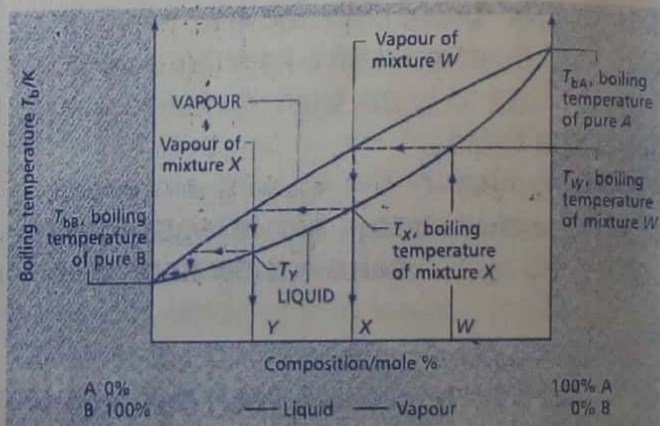
Above the upper curve, the sample has

full evaporated and the system is entirely a gas. Below the lowest curve none of the sample has evaporated and the system is entirely a liquid. Between the two curved lines the system is composed of two phases in equilibrium and we must draw the tie line to keep track of the composition of both phases.

FRACTIONAL DISTILLATION

- Is a procedure for separating liquid components of a solution based on their difference in their boiling points.
- For all mixtures of the liquids, the vapour above the mixture will contain a greater percentage of the more volatile component than will the liquid.

Consider the composition – boiling temperature for two liquid A and B when B is more volatile than A.

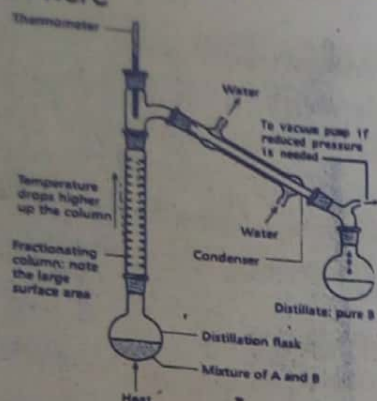


- Imagine starting with a liquid of composition W. This will boil at temperature T_w and give a vapour of composition X, which has more B and less A.
- If this vapour of composition X is condensed it will form a liquid which also has a composition of X so, by boiling and condensing, we have ended up with a liquid which is richer in B.
- This new liquid will boil at temperature T_x (lower than T_w) to give a vapour of composition Y, which condense to give a liquid of composition Y (with even more B and even less A). We could continue this process with more boiling!

condensation cycles until we reached a vapour consisting entirely of pure B. A would all be liquid.

Note

An apparatus for fractional distillation is shown here



Separating two liquids by fractional distillation

- A fractionating column produces the effect of many successful boiling/condensation cycles automatically.
- The column sides have a large surface area (see above). The mixture of A and B boils and the vapour rises up the column.
- As the temperature drops, the vapour condenses, the liquid (richer in A) drops back into the boiling flask and the vapour (richer in B) moves up the column.
- The same thing happens many times as the vapour rises up the tube. A long enough column will result in a vapour of pure B at the top of the column and eventually pure A left in the boiling point.
- Some liquid decomposes before reaching their boiling temperatures. In this case, distillation can be done under reduced pressure. Since boiling occurs when this vapour pressure of the liquid reaches external pressure, boiling then occurs at a lower temperature.

RAOULT'S LAW AS A SPECIAL CASE OF HENRY'S LAW

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by

$$P'_1 = P_1 \cdot X_1$$

- In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas, and its solubility is given by Henry's law which states that "**The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (χ) in the solution**".

i.e.

$$P = K_H \cdot \chi$$

Where

K_H = is the Henry's law constant.

- If we compare the equation for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution.
- Only the proportionality constant K_H differs from P_1 . Thus Raoult's law becomes a special case of Henry's law in which K_H becomes equal to P_1 .

EXAMPLE OF PROBLEMS INVOLVING IDEAL GAS EQUATIONS AND RAOULT'S LAW.

Qn. 88

- The ideality of the solution is approached when it is made more dilute. Explain.
- 10g of methanol give an ideal solution when mixed with 50g of ethanol. If the vapour pressure of methanol and ethanol at the same temperature are 6265Pa and 2933Pa respectively,

Calculate,

- The partial pressure exerted by each component in the mixture.
- The composition of the vapour.

Solution

- The ideality of the solution is approached when it is made more dilute because more dilute solutions have equal intermolecular forces and either association or dissociation is strongly prohibited, these conditions then favour ideal solution.
- Required: Partial pressure.

Data

$$n_{\text{meth}} = \frac{10\text{g}}{32\text{gmol}^{-1}} = 0.3125 \text{ moles}$$

$$n_{\text{eth}} = 50\text{g} = 1.087\text{moles}$$

$$46\text{g mol}^{-1}$$

$$n_T = 0.3125 + 1.087$$

$$= 1.3995\text{moles.}$$

Then,

$$\chi_{\text{meth}} = \frac{0.3125\text{mol}}{1.3995\text{mol}} = 0.223$$

Also,

$$\chi_{\text{eth}} = \frac{1.087}{1.3995} = 0.777$$

(i) From

$$P'_{\text{meth}} = \chi_{\text{meth}} \cdot P_{\text{meth}}$$

$$= 0.223 \times 6265\text{Pa}$$

$$= 1397.095\text{Pa}$$

Also

$$P'_{\text{eth}} = \chi_{\text{eth}} \cdot P_{\text{eth}}$$

$$= 0.777 \times 2933\text{Pa}$$

$$= 2278.941\text{Pa}$$

(ii) Required: Composition of vapour

For methanol

$$C_{\text{meth}} = \frac{P'_{\text{meth}}}{P_T}$$

$$C_{\text{meth}} = \frac{1397.095}{(1397.095 + 2278.941)}$$

$$C_{\text{meth}} = 0.3801 \text{ or } 38.01\%$$

Also,

$$C_{\text{eth}} = \frac{P'_{\text{eth}}}{P_T}$$

$$C_{\text{eth}} = \frac{2278.941}{(1397.095 + 2278.941)}$$

$$C_{\text{eth}} = 0.6199 \text{ or } 61.99\%$$

Qn. 89

Pentane (C_5H_{12}) and hexane (C_6H_{14}) form an ideal solution. At 25°C the vapour pressures of pentane and hexane are 511 and 150 torr, respectively. A solution is prepared by mixing 25ml pentane (density, 0.63g/ml) with 45ml hexane (density 0.66g/ml)?

(a) What is the vapour pressure of the solution?

(b) What is the composition by mole fraction of pentane in the vapour that is in equilib-

rium with this solution.

Solution

Then, gram of pentane, added.

$$\text{If } 0.63\text{g} \rightarrow 1\text{ml}$$

$$x \leftarrow 25\text{ml}$$

$$x = \frac{0.63\text{g} \times 25\text{ml}}{1\text{ml}}$$

$$x = 15.75\text{g}$$

But

$$n = \frac{m}{M_r} = \frac{15.75\text{g}}{72\text{g mol}^{-1}} = 0.23\text{moles}$$

Also, gram of hexane

$$0.66\text{g} \rightarrow 1\text{ml}$$

$$x \leftarrow 45\text{ml}$$

$$x = 29.7\text{g.}$$

But

$$n = \frac{m}{M_r} = \frac{29.7\text{g}}{86\text{g mol}^{-1}} = 0.345\text{moles.}$$

Then,

$$n_T = 0.23\text{moles} + 0.345\text{moles}$$

$$n_T = 0.575\text{moles}$$

But

$$P'_{\text{pent}} = \frac{n_{\text{pent}}}{n_T} \times P_{\text{pent.}}$$

$$P'_{\text{pent}} = \frac{0.23}{0.575} \times 511$$

$$P'_{\text{pent}} = 204.4 \text{ torr}$$

Also,

$$P'_{\text{hex}} = \frac{n_{\text{hex}}}{n_T} \times P_{\text{hex}}$$

$$P'_{\text{hex}} = \frac{0.345}{0.575} \times 150\text{torr}$$

$$P'_{\text{hex}} = 90\text{torr.}$$

(i) Required: Total pressure

Then,

$$P_T = P'_{\text{pent}} + P'_{\text{hex}}$$

$$P_T = (204.4 + 90) \text{ torr.}$$

$$P_T = 294.4\text{torr}$$

(ii) Mole fraction of pentane in vapour

i.e.

$$C_{\text{pent}} = \frac{P'_{\text{pent}}}{P_T} = \frac{204.4}{294.4} = 0.69$$

Qn. 90

The vapour in equilibrium with a pentane - hexane solution at 25°C has a mole fraction of pentane equal 0.15 at 25°C. What is the mole fraction of pentane in the solution? Given vapour pressure of pure pentane and hexane are 511torr and 150torr respectively.

Solution.

Data

Mole fraction of pentane in vapour (C_p) = 0.15

Mole fraction of hexane in vapour (C_H) = 0.85

V. pressure of pure pentane (P_p) = 511torr

V. pressure of pure hexane (P_H) = 150torr.

Let χ_p mole fraction of pentane in liquid and χ_H be mole fraction of hexane in solution.

Then $P'_{\text{pent}} = \chi_p \cdot P_p$

$$P'_{\text{pent}} = \chi_p \cdot 511 \dots\dots\dots (i)$$

Also,

$$P'_{\text{Hex}} = \chi_{\text{hex}} \cdot 150 \text{torr} \dots\dots\dots (ii)$$

But,

$$\text{Composition i.e. } C_p = \frac{P'_{\text{pent}}}{P_T} = \frac{\chi_p \cdot 511}{P_T} \dots\dots\dots (iii)$$

Also,

$$C_H = \frac{P'_{\text{Hex}}}{P_T} = \frac{\chi_{\text{Hex}} \cdot 150}{P_T} \dots\dots\dots (iv)$$

Taking ratio of eqn (iii) to eqn (iv) so as to eliminate P_T .

i.e.

$$\frac{0.15}{0.85} = \frac{\chi_p \cdot 511}{\chi_H \cdot 150}$$

$$\text{But } \chi_H = (1 - \chi_p)$$

Then,

$$\frac{0.15}{0.85} = \frac{\chi_p \cdot 511}{(1 - \chi_p) \cdot 150}$$

Now solving for χ_p above we get

$$\chi_p = 0.049.$$

Then mole fraction of pressure in liquid is 0.049

Qn. 91

Liquid Y and Z are completely miscible and form an ideal solution. A certain mixture of the two liquids boils at 410K when the pressure is 760torr. If the vapour pressure of Y at this temperature is 862.78torr and that of Z is 453.15 torr. Calculate the mole fraction of Y in the

(i) Liquid mixture (ii) vapour mixture

Solution

From

$$P_T = P_Y \cdot \chi_Y + P_Z \cdot \chi_Z \dots\dots\dots (i)$$

But

$$C_Y = \frac{P'_Y}{P_T} = \frac{P_Y \cdot \chi_Y}{P_T} \dots\dots\dots (ii)$$

And

$$C_Z = \frac{P'_Z}{P_T} = \frac{P_Z \cdot \chi_Z}{P_T} \dots\dots\dots (iii)$$

From first equation.

$$\begin{cases} 760 = 862.78\chi_Y + 453.15\chi_Z \\ 1 = \chi_Y + \chi_Z \end{cases}$$

Solve the two equations simultaneously, we get

$$\chi_Y = 0.75$$

$$\chi_Z = 0.25$$

From

Composition of Y = $\frac{\text{Partial pressure of Y}}{\text{Total pressure}}$

i.e.

$$C_Y = \frac{P'_Y}{P_T} = \frac{\chi_Y \cdot P_Y}{P_T}$$

$$C_Y = \frac{0.75 \times 862.78}{760}$$

$$C_Y = 0.85$$

Then mole fractions of y in liquid and vapour are 0.75 and 0.85 respectively.

Qn. 92

At 333K substance A has a vapour pressure of 1.0atm and substance B has a vapour pressure of 0.2atm. A solution of A and B is prepared and allowed to equilibrate with its vapour. The vapour is found to have equal moles of A and B. If the solution shows ideal behaviours what are the mole fractions of A and B in the original solutions?

Solution

From Raoult's law,

$$P'_A = \chi_A \cdot P_A$$

And

$$P'_B = \chi_B \cdot P_B$$

- Equal moles of A and B in vapour shows that,

$$P'_A = P'_B$$

Then,

$$\chi_A \cdot P_A = \chi_B \cdot P_B$$

- Let mole fraction of A i.e. χ_A be x so that χ_B be $1 - x$.

Then

$$x(1.0) = (1 - x)(0.2)$$

$$x = 0.2 - 0.2x$$

$$\frac{1.2x}{1.2} = \frac{0.2}{1.2}$$

$$x = 0.17$$

(This is mole fraction of A) then mole fraction of B is $1 - 0.17 = 0.83$

Qn. 93

When benzene (C_6H_6) and toluene (C_7H_8) are mixed they form an ideal solution.

- (i) At 80°C the vapour pressure of benzene is 753 torr and that of toluene is 290 torr if 24g of benzene and 61.3g of toluene are mixed what is the total vapour pressure above the mixture?
- (ii) What is the composition of the vapour over the solution of 24g of benzene and 61.3g toluene?

Solution

Data

$$P_{Benz} = 753 \text{ torr.}$$

$$P_{tol} = 290 \text{ torr.}$$

$$n_{Benz} = \frac{m}{Mr} = \frac{24}{78 \text{ gmol}^{-2}} = 0.31 \text{ moles}$$

$$n_{tol} = 0.67 \text{ moles}$$

$$n_T = (0.31 + 0.67) \text{ moles} = 0.98 \text{ moles}$$

(i) Required: Total vapour pressure.

1st case:

Find the partial vapour pressure of benzene from the above data.

$$P'_{Benz} = \frac{n_{Benz}}{n_T} \times P_{Benz}$$

$$\text{i.e. } P'_{Benz} = \frac{0.31 \text{ moles}}{0.98 \text{ moles}} \times 753 \text{ torr}$$

$$P'_{Benz} = \frac{0.31 \text{ moles}}{0.98 \text{ moles}} \times 753 \text{ torr}$$

$$P'_{Benz} = 238.2 \text{ torr}$$

Hence the partial vapour pressure of benzene is 238.2 torr

2nd case:

Find the partial vapour pressure of toluene from the data above.

i.e.

$$P'_{tol} = \chi_{tol} \times P_{tol}$$

$$P'_{tol} = \frac{0.67 \text{ moles}}{0.98 \text{ moles}} \times 290 \text{ torr}$$

$$P'_{tol} = 198.3 \text{ torr.}$$

Hence the partial vapour pressure of toluene is 198.3 torr.

3rd case:

Total vapour pressure is obtained from Dalton's law of partial pressure.

i.e.

$$P_T = P_{Benz} + P_{tol}$$

$$P_T = (238.2 + 198.3) \text{ torr}$$

$$P_T = 436.5 \text{ torr}$$

(ii) Required: Composition of the vapour.

For benzene,

$$C_{\text{Benz}} = \frac{P_{\text{Benz}}}{P_T}$$

$$C_{\text{Benz}} = \frac{238.2}{436.5}$$

$$= 0.55 \text{ or } 55\%$$

For toluene,

$$1 - 0.55 = 0.45 \text{ or } 45\%$$

Hence the composition of the vapour over the solution of 24g of benzene and 61.3g of toluene are 0.55 or 55% benzene and 0.45 or 45% toluene.

Qn. 94

An ideal solution is prepared from 2 moles of benzene and 3 moles of toluene at 437°C. At the same temperature the vapour pressure of benzene is 53 N/m² and that of toluene is 26.7 N/m² calculate,

- Partial vapour pressure of each component.
- Total vapour pressure

If the mixture solution above is distilled which substance will be collected from the top of the distillation column?

Solution

Data

$$n_{\text{Benz}} = 2 \text{ mole}$$

$$n_{\text{tol}} = 3 \text{ mole}$$

$$P_{\text{Benz}} = 53 \text{ N/m}^2$$

$$P_{\text{tol}} = 26.7 \text{ N/m}^2$$

$$n_r = 5 \text{ mole}$$

- Required: Partial pressure of each component

For benzene,

$$P'_{\text{Benz}} = \frac{n_{\text{Benz}}}{n_T} \times P_{\text{Benz}}$$

$$P'_{\text{Benz}} = 0.4 \times 53 \text{ N/m}^2$$

$$P'_{\text{Benz}} = 21.2 \text{ N/m}^2$$

Then partial pressure of benzene is 21.2 N/m²

For toluene,

$$P'_{\text{tol}} = \frac{n_{\text{tol}}}{n_T} \times P_{\text{tol}}$$

$$P'_{\text{tol}} = 0.6 \times 26.7$$

$$P'_{\text{tol}} = 16.02 \text{ N/m}^2$$

Then partial pressure of toluene is 16.02 N/m²

Required: Total vapour pressure from Dalton's law of partial pressure

$$P_T = P_{\text{Benz}} + P'_{\text{tol}}$$

$$= 21.2 \text{ N/m}^2 + 16.02 \text{ N/m}^2$$

$$= 37.22 \text{ N/m}^2$$

Hence the total vapour pressure is 37.22 N/m²

If the mixture solution above is distilled benzene will be collected from the top of the distillation column, due to the fact that benzene has greater tendency to form vapour above its surface than toluene this is because at the same temperature benzene forms more vapour (53 N/m²) than ~~volume~~ ^{toluene} (26.7 N/m²)

Qn. 95

An ideal solution containing solvent x and y boils at 98°C. If the mole fraction of y in the vapour is 0.58. what is the mole fraction of x in the liquid? Given at 98°C the vapour pressure of pure x and y are 290 torr and 95 torr respectively (1 torr = 1 mmHg)

Solution

Data

$$\text{Mole fraction of y in vapour} = 0.58$$

$$\text{Mole fraction of x in vapour} = 0.42$$

$$\text{Vapour pressure of pure x} = 290 \text{ torr}$$

$$\text{Vapour pressure of pure y} = 95 \text{ torr}$$

Required: Mole fraction of x in the liquid.
Let x_a be mole fraction of x in liquid and y_b be mole fraction of y in liquid.

Then

$$P'_x = x_a \cdot P_x \dots \dots \dots (i)$$

Also,

$$P'_y = y_b \cdot P_y \dots \dots \dots (ii)$$

From composition of vapour

Compositions of x = $\frac{\text{Partial pressure of x}}{\text{Total pressure}}$

$$C_x = \frac{P'_x}{P_T}$$

But $P'_x = x_a \cdot P_x$ from eqn (i).

i.e.

$$C_x = \frac{x_a \cdot 290}{P_T}$$

$$0.42 = \frac{x_a \cdot 290}{P_T} \dots \dots \dots (iii)$$

Also $C_y = \frac{p'_y}{P_T}$

$$0.58 = \frac{y_b \cdot 95}{P_T} \dots \dots \dots (iv)$$

Taking ratio of equation (iii) and (iv) so as to eliminate total pressure (P_T)

i.e.

$$\frac{0.42}{0.58} = \frac{x_a \cdot 290}{y_b \cdot 95}$$

Or

$$\frac{0.42}{0.58} = \frac{x_a \cdot 290}{(1 - x_a) \cdot 95}$$

Solve for x

$$\frac{0.72}{1} = \frac{x_a \cdot 290}{(1 - x_a) \cdot 95}$$

$$290x_a = 68.8 - 68.8x_a$$

$$290x_a + 68.8x_a = 68.8$$

$$\frac{358.8 x_a}{358.8} = \frac{68.8}{358.8}$$

$$x_a = 0.2$$

Hence the mole fraction of x in liquid is 0.2

Qn. 96

Heptane and Octane form essentially ideal solution. A particular solution containing 2 moles of heptane and 3 moles of octane has total vapour pressure of 280mmHg at 60°C. When one mole of heptane was added to the solution above, the total vapour pressure at the same temperature was measured to 300mmHg. Calculate vapour pressure exerted by pure heptane and octane at 60°C

Solution

Data

1st case: Before addition of one mole

$$n_{\text{Hep}} = 2 \text{ mole}$$

$$n_{\text{Oct}} = 3 \text{ mole}$$

$$n_T = 5$$

$$\chi_{\text{He}} = \frac{2}{5} = 0.4$$

$$\chi_{\text{Oct}} = \frac{3}{5} = 0.6$$

$$P_T = 280 \text{ mmHg}$$

$$280 = 0.4P_{\text{He}} + 0.6P_{\text{Oct}}$$

$$280 = 0.4P_{\text{He}} + 0.6P_{\text{Oct}} \dots \dots \dots (i)$$

2nd Case: After addition of 1 mole

$$n_{\text{He}} = 3 \text{ Moles}$$

$$n_{\text{Oct}} = 3 \text{ moles}$$

$$\chi_{\text{He}} = \frac{3}{6} = 0.5$$

$$\chi_{\text{Oct}} = \frac{3}{6} = 0.5$$

$$P_T = 300 \text{ mmHg}$$

But

$$P_T = P'_{\text{He}} + P'_{\text{Oct}}$$

$$300 = 0.5P_{\text{He}} + 0.5P_{\text{Oct}} \dots \dots \dots (ii)$$

Now from eqn. (i) and (ii) we get

$$\begin{cases} 0.4P_{\text{He}} + 0.6P_{\text{Oct}} = 280 \\ 0.5P_{\text{He}} + 0.5P_{\text{Oct}} = 300 \end{cases}$$

Solve for P_{He} and P_{Oct} simultaneously

i.e. $P_{\text{He}} = 400\text{mmHg}$
 $P_{\text{oct}} = 200\text{mmHg}$

Hence the vapour pressure of pure heptane and octane are 400mmHg and 200mmHg respectively.

Qn. 97

A solution is prepared from 2g of carbon disulphide (CS_2) and 5g of thionyl chloride (SOCl_2) at 70°C . The partial vapour pressure of the components above solution were measured and found to be 371mmHg for CS_2 and 233mmHg for SOCl_2 . The vapour pressure of pure CS_2 is 560mmHg and that of SOCl_2 is 446mmHg. Is the mixture solution above ideal? Account for your answer.

Solution

Data

$$n_{\text{CS}_2} = \frac{2\text{g}}{76\text{gmol}^{-1}} = 0.026\text{moles}$$

$$n_{\text{SOCl}_2} = \frac{5\text{g}}{119\text{gmol}^{-1}} = 0.042$$

$$n_T = 0.068\text{ moles}$$

$$P_{\text{CS}_2} = 560\text{mmHg}$$

$$P_{\text{SOCl}_2} = 446\text{mmHg}$$

1st Case:

Calculate the partial vapour pressure expected from ideal solution by applying Raoult's law.

For CS_2

$$P'_{\text{CS}_2} = \frac{n_{\text{CS}_2}}{n_{\text{CS}_2} + n_{\text{SOCl}_2}} \times P_{\text{CS}_2}$$

$$P'_{\text{CS}_2} = \frac{0.026}{0.068} \times 560\text{mmHg}$$

$$P'_{\text{CS}_2} = 214\text{mmHg}$$

For SOCl_2

$$P'_{\text{SOCl}_2} = \frac{n_{\text{SOCl}_2} \times P_{\text{SOCl}_2}}{n_T}$$

$$P'_{\text{SOCl}_2} = 275.5\text{mmHg}$$

2nd case

Compare the calculated partial vapour pressures from Raoult's law and the measured partial vapour pressures.

The calculated partial vapour pressures are different from the measured partial vapour pressure. This indicates that the solution above is non-ideal.

Conclusion:

Had the solution being ideal the calculated partial vapour pressure from Raoult's law would be exactly the same as the measured partial vapour pressure. Hence the solution above does not obey the Raoult's law.

Qn. 98

13g of benzene were mixed with 18g of toluene at 100°C . At this temperature pure benzene has vapour pressure of 10atm and toluene exerts 6atm pressure.

If benzene-toluene mixture was distilled what would be the composition of the 3rd distillate?

Solution

1st case:

Calculate the composition of the vapour above original solution.

Data

$$n_B = \frac{13\text{g}}{78\text{gmol}^{-1}} = 0.17\text{moles}$$

$$n_t = \frac{18\text{g}}{92\text{gmol}^{-1}} = 0.2\text{ moles}$$

$$n_T = 0.37\text{ moles}$$

$$P_B = 10\text{atm}$$

$$P_t = 6\text{atm}$$

For benzene

$$P'_B = \frac{n_B}{n_T} \times P_B$$

$$P'_B = \frac{0.17 \times 10}{0.37}$$

$$P'_B = 4.6 \text{ atm}$$

For toluene

$$P'_t = \frac{n_t \times P_t}{n_T}$$

$$P'_t = \frac{0.2 \times 6}{0.37}$$

$$P'_t = 3.24 \text{ atm}$$

Then

$$P_T = 4.6 \text{ atm} + 3.24 \text{ atm} = 7.84 \text{ atm}$$

Compositions of vapour

For benzene

$$C_B = \frac{P'_B}{P_T} = \frac{4.6}{7.84}$$

$$C_B = 0.59$$

For toluene

$$C_t = 1 - 0.59 = 0.41$$

Hence composition of vapour above original solution is 0.59 benzene and 0.41 toluene. When this vapour is condensed a first distillate is obtained. Composition of the first distillate, will be the same as composition of vapour i.e. 0.59 benzene and 0.41 toluene.

2nd case:

Calculate composition of vapour above the first distillate when boiled.

Data:

$$\chi_B = 0.59$$

$$\chi_t = 0.41$$

$$P_B = 10 \text{ atm}$$

$$P_t = 6 \text{ atm}$$

Then,
For benzene

$$P'_B = \chi_B \cdot P_B$$

$$P'_B = 0.59 \times 10$$

$$P'_B = 5.9 \text{ atm}$$

For toluene

$$P'_t = \chi_t \cdot P_t$$

$$P'_t = 0.41 \times 6$$

$$P'_t = 2.46 \text{ atm}$$

Then

$$P_T = P'_B + P'_t = (5.9 + 2.46) \text{ atm} = 8.36 \text{ atm}$$

Composition of vapour

For benzene

$$C_B = \frac{P'_B}{P_T}$$

$$C_B = \frac{5.9}{8.36}$$

$$C_B = 0.71$$

For toluene

$$C_t = 1 - 0.71 = 0.29$$

Hence compositions of vapour above first distillate is 0.71 benzene and 0.29 toluene when this vapour is condensed a second distillate is obtained with the same composition i.e. 0.71 benzene and 0.29 toluene.

3rd case: Calculate the composition of vapour above second distillate when boiled.

i.e.

$$\chi_B = 0.71$$

$$\chi_t = 0.29$$

$$P_B = 10 \text{ atm}$$

$$P_t = 6 \text{ atm}$$

For benzene

$$P'_B = \chi_B \cdot P_B$$

$$P'_B = 0.71 \times 10 \text{ atm} = 7.1 \text{ atm}$$

For toluene

$$P'_t = \chi_t \cdot P_t$$

$$P'_t = 0.29 \times 6 \text{ atm}$$

$$P'_t = 1.74 \text{ atm}$$

Then

$$P_T = P'_B + P'_T$$

$$P_T = 7.1\text{atm} + 1.74\text{atm}$$

$$= 8.84\text{atm}$$

Composition of vapour

For benzene

$$C_B = \frac{P'_B}{P_T}$$

$$C_B = \frac{7.1}{8.84}$$

$$C_B = 0.8$$

For toluene

$$C_t = 1 - 0.8$$

$$C_t = 0.2$$

Conclusion

Hence composition of vapour above second distillate is 0.8 or 80% benzene and 0.2 or 20% toluene. When this vapour is condensed third distillate is obtained. The composition of third distillate is thus the same as composition of vapour i.e 80% benzene and 20%.

Qn. 99

A particular ideal solution is made by mixing 1, 1 - Dichloroethane (CH_3CHCl_2) and 1, 1 - Dichlorotetrafluoroethane ($\text{CF}_3\text{CCl}_2\text{F}$). At 25°C 1,1 Dichloroethane was found to have vapour pressure of 228torr and at the sample temperature Dichlorotetrafluoroethane exerts 79torr. What mass of 1, 1 - dichloroethane must be mixed with 240g of 1, 1 dichlorotetrafluoroethane to give a solution with vapour pressure 157torr at 25°C ?

Solution

Let Cl be the first compound and F the second

Then,

$$P_T = P'_{Cl} + P'_F$$

Or

$$P_T = \chi_{Cl} \cdot P_{Cl} + \chi_F \cdot P_F$$

Substitute the known values

$$157 = (x) 228 + (1-x) 79$$

$$157 = 228x + 79 - 79x$$

$$157 - 79 = 228x - 79x$$

$$\frac{78}{149} = \frac{149x}{149}$$

$$x = 0.52 \text{ (this is mole fraction of Cl)}$$

But the mole fraction = $\frac{\text{number of moles of Cl}}{\text{Total number of moles.}}$

$$0.52 = \frac{x}{99} \div \left(\frac{x}{99} + \frac{240}{170} \right)$$

$$\text{Or } 0.48 = \frac{240}{170} \div \left(\frac{240}{170} + \frac{x}{99} \right)$$

Solve in any case algebraically,

Case 2

$$\frac{0.48}{1} = \frac{240}{170} \times \left(\frac{16830}{27360 + 170x} \right)$$

$$\frac{0.48}{1} = \left(\frac{4039200}{4039200 + 28900x} \right)$$

$$4039200 = 1938816 + 13872x$$

$$4039200 - 1938816 = 13872x$$

$$\frac{2100384}{13872} = \frac{13872x}{13872}$$

$$x = 151.4\text{g}$$

Qn. 100

Benzene (C_6H_6) and toluene (C_7H_8) are two hydrocarbons that form a very nearly ideal solution. At 300K the vapour pressure of pure benzene is 160mmHg. Assuming an ideal solution behavior; Calculate the partial pressures of benzene and toluene and the total pressure over the following solutions.

- One made by combining equal number of benzene and toluene molecule.
- One made by combining equal masses of benzene and toluene.

NON-IDEAL SOLUTIONS.

What is non ideal solution?

- Is a solution formed from completely miscible solvents and whose intermolecular forces in solution are different from inter-molecular forces of their pure solvents and such solution does not obey Raoult's law.
- This means that partial vapour pressure of the component above non-ideal solution can not be calculate in accordance to Raoult's law.
- Non ideal solution is said to deviate form Raoult's law.

TYPES OF NON-IDEAL SOLUTIONS

- There are two types of non-ideal solutions. The classification of these depends on how they deviate from Raoult's law.
 - (a) Non ideal solutions which deviate positively form Raoult's law.
 - (b) Non ideal solutions which deviate negatively from Raoult's law.

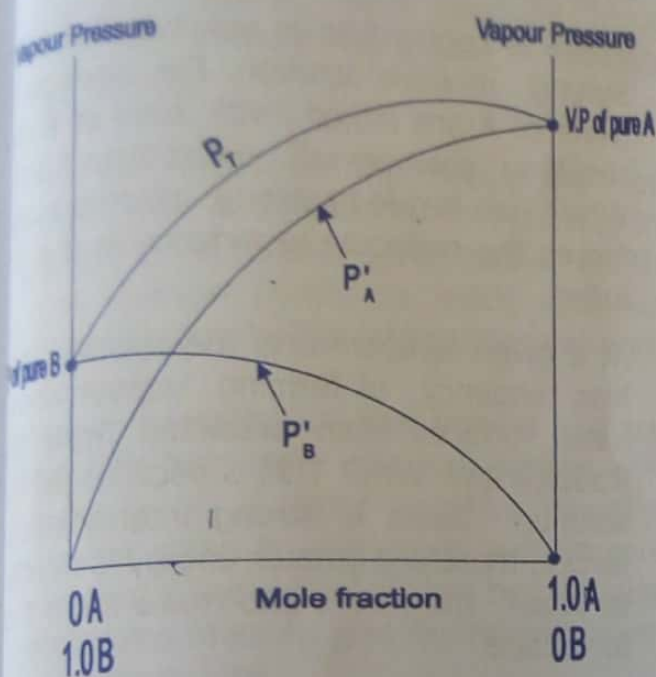
(a) NON IDEAL SOLUTIONS OF POSITIVE DEVIATIONS.

- Non ideal solutions of positive deviations are those in which the inter-molecular forces existing in solution are less strong than inter-molecular forces of their pure solvent.
- Non-ideal solutions which deviate positively from Raoult's law have the following properties: -
 - The heat of solution is positive (endothermic). This means that mixing is endothermic process.
 - There is expansion of the volume of the resulting mixture solution. For example if 30cm^3 of solvent A is mixed with 20cm^3 of solvent B, the volume of the resulting mixture solution will be greater

than 50cm^3 . why? This is because the molecules are attracted with less inter-molecular forces than when they were in their respective pure solvents in the solution, the molecules spread far apart away from each other and occupy large space.

- At a given temperature a solution has greater tendency of forming vapour pressure than expected from Raoult's law. Hence the name positive deviation.) Why?
 - This is due to weak intermolecular forces between unlike molecules. Low amount of energy is just needed to break the intermolecular forces and set the molecules free to escape .
 - Generally positive deviations occur for two reasons:
 - (i) First of all, attractions or bonding between molecules of components A and B are weak. Bonding between molecules of components A and B are represented by A.....B.
 - (ii) Secondly, bonding of the A.....A and B B types are broken on mixing the two components. These bonds are often hydrogen bonds.
 - When non ideal solution are distilled at one composition they form azeotropic (constant boiling) mixture which boil at lower temperature than boiling point of the pure solvent.
 - **Azeotropic mixture:** Is a solution which boil at constant temperature and give vapour above its surface which has the same composition as the liquid itself.

VAPOUR PRESSURE COMPOSITION CURVE FOR NON IDEAL SOLUTION OF POSITIVE DEVIATION.



BOILING POINT - COMPOSITION DIA- GRAM FOR NON-IDEAL SOLUTION OF POSITIVE DEVIATION.

Recall that a large positive deviation from Raoult's law produces a vapour pressure curve with a maximum value at same composition other than pure A or B.

If a mixture has a high vapour pressure it means that it will have a low boiling point. The molecules are escaping easily and you won't have to heat the mixture much to overcome the intermolecular attractions completely.

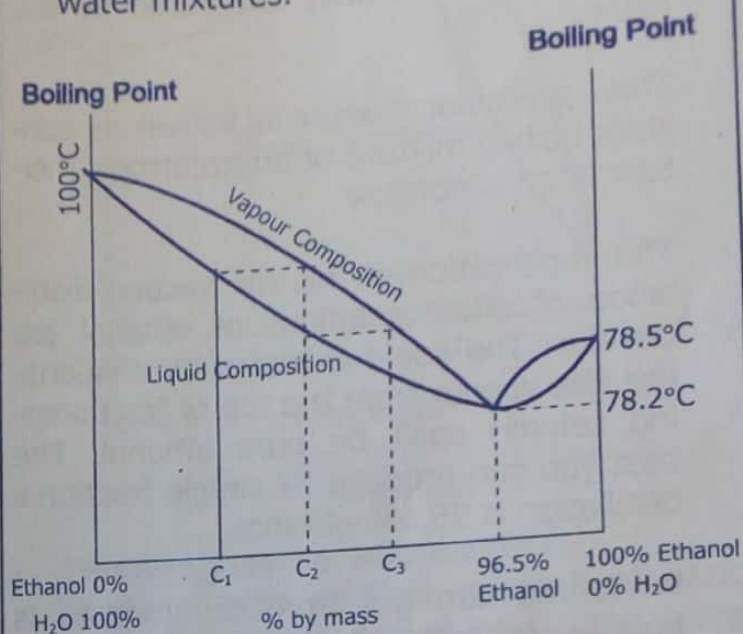
The implication of this is that the boiling point (composition curve) will have a minimum value lower than the boiling point of either A or B.

In the case of the mixture of ethanol and water this minimum occurs with 95.6% by mass ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C and water at 100°C.

You might think that this difference 0.3°

C doesn't matter much, but it has huge implications for the separation of ethanol-water mixtures.

- The diagram below shows the boiling point-composition curve for ethanol-water mixtures.



- From the graph above, suppose you are going to distil a mixture of ethanol and water with composition C_1 as shown above. It will boil at a temperature given by the liquid curve and produce vapour with composition C_2 .
- When that vapour condenses it will, of course still have the composition C_2 . If you re-boil that, it will produce a new vapour with composition C_3 .
- You can see that if you carried on with this boiling - condensing re-boiling sequence, you would eventually end up with a vapour with a composition of 95.6% ethanol. If you condense that you obviously get a liquid with 95.6% ethanol.

Qn. What happens if you boil that liquid?

- The liquid curve and the vapor curve meet at that point. The vapour produced will have that same composition of 95.6% ethanol. If you condense it again, it will still have that same composition.
- You have hit a barrier. It is impossible to get pure ethanol by distilling any mixture

of ethanol and water containing less than 95.6% of ethanol.

- This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapour composition is exactly the same as the liquid.
- This particular mixture is known as constant boiling mixture or an azeotropic mixture or an azeotrope
- The implication of this for fraction distillation of dilute solutions of ethanol are obvious. The liquid collected by condensing the vapour from the top of fractionating column can't be pure ethanol. The best you can produce by simple fractional distillation is 95.6% ethanol.
- What you can get from the mixture is pure water. As ethanol rich vapor is given off from the liquid boiling in the distillation flask. It will eventually lose all the ethanol to leave just water.

To summarize:-

- * Distilling a mixture of ethanol containing less than 95.6% of ethanol by mass lets you collect.
 - A distillate containing 95.6% of ethanol in the collecting flask.
 - Pure water in the boiling flask
- * Distilling a mixture of ethanol containing more than 95.6% ethanol by mass lets you collect.
 - A distillate containing 95.6% ethanol in the collecting flask.
 - Pure ethanol in the boiling flask.

(b) NON IDEAL SOLUTIONS OF NEGATIVE DEVIATIONS

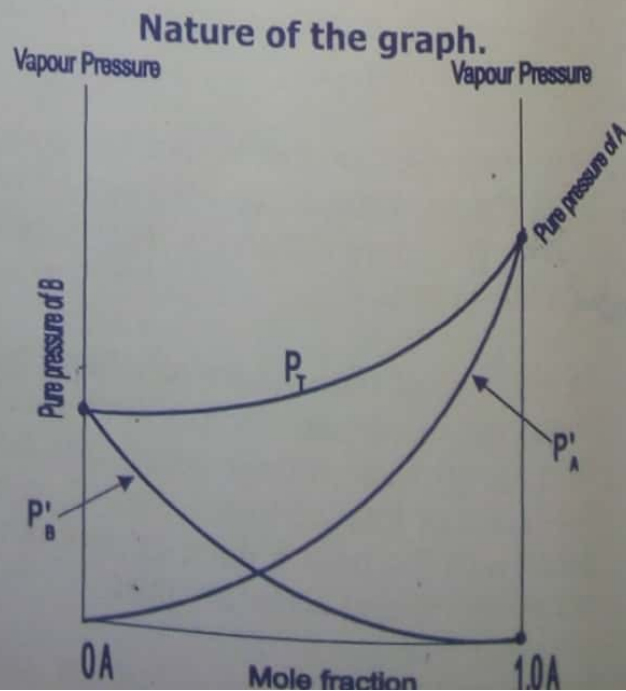
- Non ideal solutions of negative deviation are those solutions whose intermolecular forces existing in solution are different from those existing in pure solvents.
- Non ideal solutions of negative deviations

have the following properties.

- The heat of solution is negative i.e. Mixing is an exothermic process.
- There is contraction in volume of the resulting mixture solution. For example if 30ml of A are mixed with 20ml of B the resulting solution will be less than 50ml. Why? This is due to strong intermolecular forces the molecule experience in the solution.
- At a given temperature, the solution has less tendency of forming vapour above their surfaces than predicted from the Raoult's law. Why? This is because in the solution there is strong intermolecular forces, therefore greater energy is needed to break the forces and make them free to escape.
- Non ideal solutions when are distilled, they form azeotropic mixture which boils at relatively higher temperature than boiling points of the pure solvent.

VAPOUR PRESSURE COMPOSITION CURVE FOR NON IDEAL SOLUTION OF NEGATIVE DEVIATION.

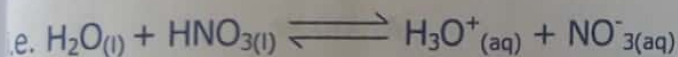
- In plotting this graph, we have to lower any line curves ponding to pressure from Raoult's law pressure. This shows that vapour pressure formed under negative deviation is always less than expelled from Raoult's law.



The reason for deviation above is that the molecules break away from the mixture less easily (difficultly) than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

You can recognize this happening because heat is evolved when you mix the liquids—more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

Many examples of this involve actual reaction between the two liquids. The example of a major negative deviation we are going to discuss is a mixture of nitric acid and water. These two covalent molecules react to give hydroxonium ions and nitrate ions.



You now have strong ionic attractions involved

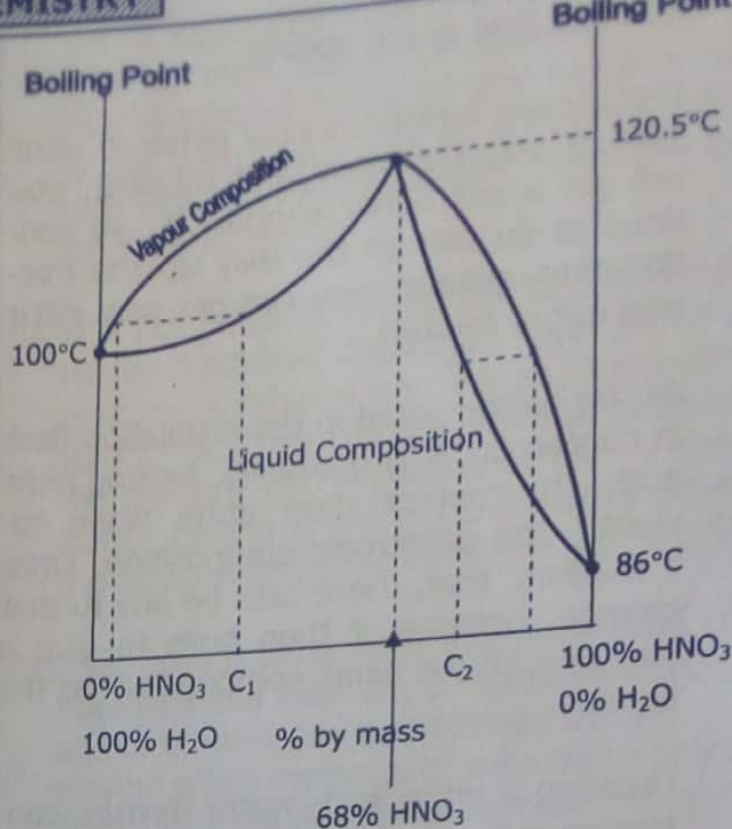
BOILING POINT-COMPOSITION DIAGRAM FOR NON IDEAL SOLUTION OF NEGATIVE DEVIATIONS

Nitric acid and water form mixtures in which particles break away to form the vapour with much more difficulty than in either of the pure liquids.

This means that mixture of nitric acid and water can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger attractions in the mixture.

In the case of mixtures of nitric acid and water there is a maximum boiling point of 120.5°C when the mixture contains 68% by mass of nitric acid. This compares with the boiling point of pure nitric acid at 86°C , and water at 100°C .

Notice the much bigger difference this time due to the presence of the new ionic interactions.



* Distilling dilute nitric acid.

- Starting with a dilute solution of nitric acid with a composition of C₁ and trace through what happens.
- The vapour produced is richer in water than the original acid. If you condense the vapour and reboil it, the new vapour is even richer in water. Fractional distillation of dilute nitric acid will enable you to collect pure water from the top of the fractionating column.
- As the acid loses water, it becomes more concentrated. Its concentration gradually increases until it gets to 68% by mass of nitric acid. At that point the vapour produced has exactly the same concentration as the liquid, because the two curves meet.
- You produce a constant boiling mixture (or azeotropic mixture or azeotrope). If you distill dilute nitric acid, you can't produce pure nitric acid from the dilute acid by distilling it.
- Distilling nitric acid more concentrated than 68% by mass
- This time you are starting with a concentration C₂ to the right of the azeotropic

mixture. (see graph above).

- The vapour formed is now richer in nitric acid. If you condense and reboil it, you will get a still richer vapour. If you continue to do this all the way up the fractionating column, you can get pure nitric acid out of the top.
- As far as the liquid in the distillation flask is concerned, it is gradually losing nitric acid. Its concentration drifts down towards the azeotropic composition. Once it reaches that, there can't be any further change, because it then boils to give a vapour with the same composition as the liquid.
- Distilling a nitric acid-water mixture containing more than 68% by mass of nitric acid gives you pure nitric acid from the top of the fractionating column and azeotropic mixture left in the distillation flask.
- **Note:** Each pair of non ideal solution has its specific composition in which it forms azeotropic mixture.

- When non ideal solutions of positive deviation are distilled, they tend to give vapour above their surface which is richer in one component and deficiency of the other component such that the vapour collected should attain azeotropic composition.

- Non ideal solutions of negative deviations when are distilled, they tend to give vapour above their surface which is richer in one component and deficiency of the other component such that the residual solution which remain behind should attain azeotropic composition.

Once azeotropic composition is attained an equilibrium is established between vapour and liquid. At equilibrium the number of molecules escaping from the

liquid and go into vapour becomes equal to the number of molecules which condense in the vapour and drop into liquid.

- This makes the composition of vapour it remain constant.
- The distillate obtained by condensation of this vapour of constant composition will be azeotropic mixture.
- Due to their behavior of forming azeotropic mixture during distillation process non ideal solution can not be separated to their pure solvents by fractional distillation method.

Qn.

How can azeotropic mixture be separated to their pure components?

Answer

- Azeotropic mixture can be separated to their pure components by applying other methods of separating the mixture apart from fractional distillation method.
- The common method of separation is the use of suitable drying agents like CaO-quick lime) which combines with water to form Ca(OH)_2 or use of silica gel.

Qn.

Why are azeotropic mixtures not regarded as compound?

Answer

Because their compositions vary with the distillation pressure.

EXAMPLE OF PROBLEMS ON RAULTS LAW AND NON-IDEAL SOLUTIONS.

Qn. 101

Ethanol and water form an azeotropic mixture which boils at 78.1°C containing 95.6% ethanol at standard pressure. The boiling point of pure water and pure ethanol are 100°C and 78.4°C respectively,

(i) Draw a temperature versus mole fraction phase diagram of the ethanol – water solution.

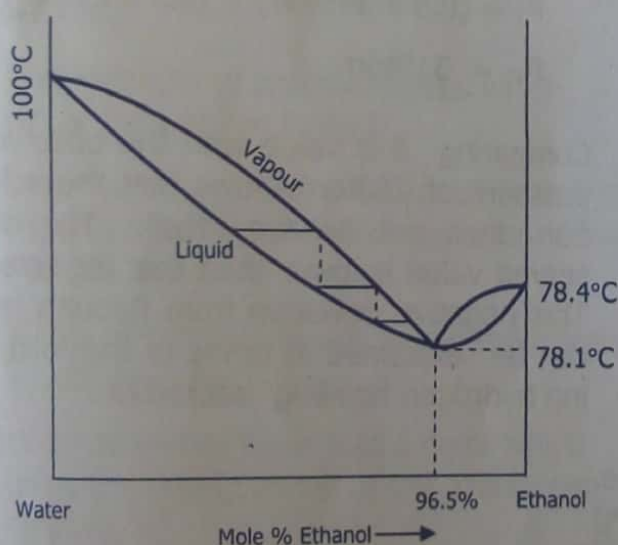
(ii) Explain what happens when a dilute aqueous ethanol solution of less than 50% and a concentrated aqueous ethanol solution of more than 96% are boiled separately in beakers.

(iii) Why is it not possible to get 100% pure ethanol by fraction distillation method of a mixture of ethanol and water which contains less than 95.6% ethanol?

(iv) After having obtained a 95.6% ethanol – water mixture how would you get a higher percentage of ethanol solutions?

Solution

(i)



(ii) When a dilute aqueous ethanol solution of less than 50% is boiled separately in a beaker will give vapour which is richer in ethanol than water until all the ethanol has gone and composition of vapour reaches 95.6% ethanol. In this case water will be left pure in the distillation flask. Also ethanol will be collected at the receiver containing azeotropic mixture of 95.6% ethanol.

On the other hand when a concentrated aqueous ethanol, of more than 96% etha-

nol is separately boiled in a beaker will give vapour above its surface until a 95.6% ethanol has gone and be collected at the collecting flask as azeotropic mixture and in the distillation flask will be left pure ethanol.

(iii) It is not possible to get 100% pure ethanol by fractional distillation method of a mixture of ethanol and water which contains less than 95.6% ethanol because the mixture on distillation forms a constant boiling mixture (azeotropic) when the composition of ethanol reaches 95.6%

(iv) After having obtained a 95.6% ethanol in ethanol water mixture, a higher percentage of ethanol can be obtained by employing other methods of separation apart from fractional distillation method these methods are

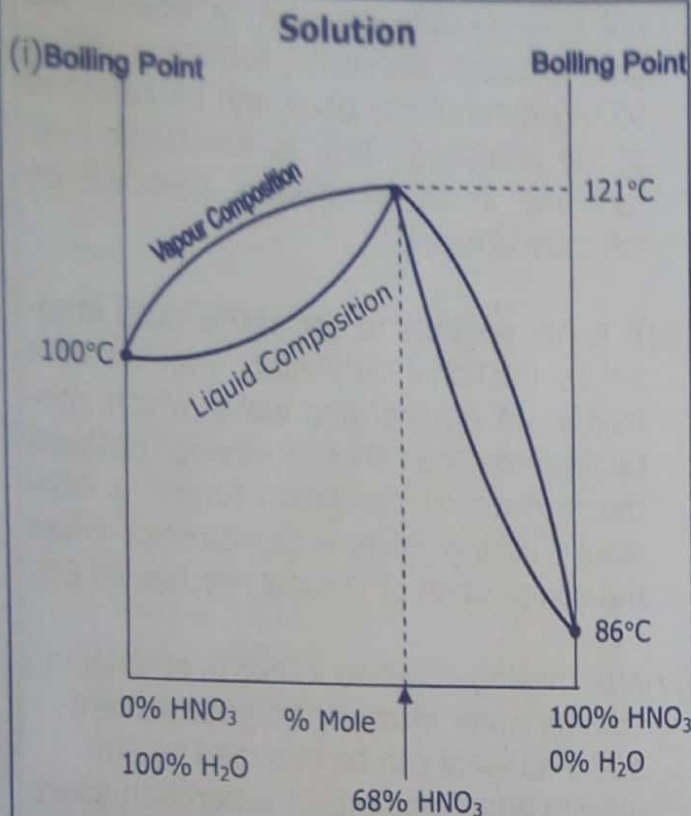
- ♦ Use of powerful drying agents e.g. Quicklime
- ♦ Solvent extraction.

Qn. 102

Nitric acid solution forms azeotropic mixture which contains 68% HNO_3 and which boils at 121°C pure water and nitric acid boil at 100°C and 86°C respectively.

(i) Sketch temperature mole fraction phase graph for this solution

(ii) What will happen when dilute solution containing less than 50% HNO_3 and concentrated solution of more than 70% are separately boiled in a beaker.



(ii) When dilute solution containing less than 50% HNO₃ is boiled, the vapour will be richer in water molecules than HNO₃. If you condense the vapour and reboil the new vapour will be even richer in water. The concentration of HNO₃ in liquid will gradually increase until the composition of HNO₃ reaches 68% when azeotropic mixture is formed.

- On the other hand if a concentrated solution of more than 70% nitric acid is boiled will give vapour above its surface which contains more nitric acid molecules than water molecules until the composition of the residual solution reaches 68.2% HNO₃ when azeotropic mixture is formed.

Qn. 103

A solution is prepared by mixing 5.81g of acetone (C₃H₆O) and 11.9g chloroform (CHCl₃). At 35°C this solution has a total vapour pressure of 260 torr. Is this an ideal solution. The vapour pressure of pure acetone and pure chloroform at 35°C are 345 and 293 torr.

Solution

1st case

Let us find the expected total vapour pressure from Raoult's law

i.e.

$$P_T = \chi_A \cdot P_A + \chi_C \cdot P_C$$

Where A stands for acetone and C for chloroform

- The calculated value can then be compared to the observed vapour pressure.

But,

$$n_A = \frac{5.81g}{58.1g/mol} = 0.1 \text{ moles}$$

$$n_C = \frac{11.9g}{119g/mol} = 0.1 \text{ moles}$$

Since the solution contains the same number of moles of acetone and chloroform then,

$$\chi_A = 0.5$$

And $\chi_C = 0.5$

Thus, the expected vapour pressure is

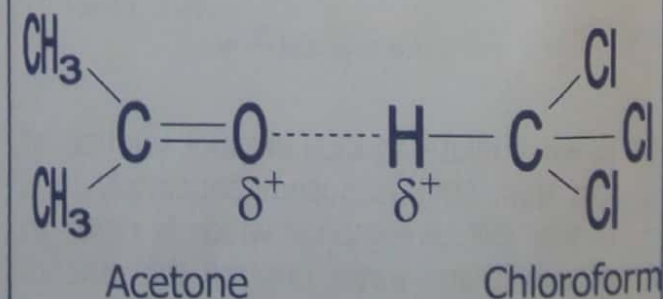
$$P_T = \chi_A \cdot P_A + \chi_C \cdot P_C$$

$$P_T = (0.5 \times 345 \text{ torr}) + (0.5 \times 293 \text{ torr})$$

$$P_T = 319 \text{ torr.}$$

- Comparing this value with the observed pressure of 260 torr shows that the solution does not behave ideally. The observed value is lower than that expected. This negative deviation from Raoult's law can be explained in terms of the following hydrogen bonding interaction.

i.e.

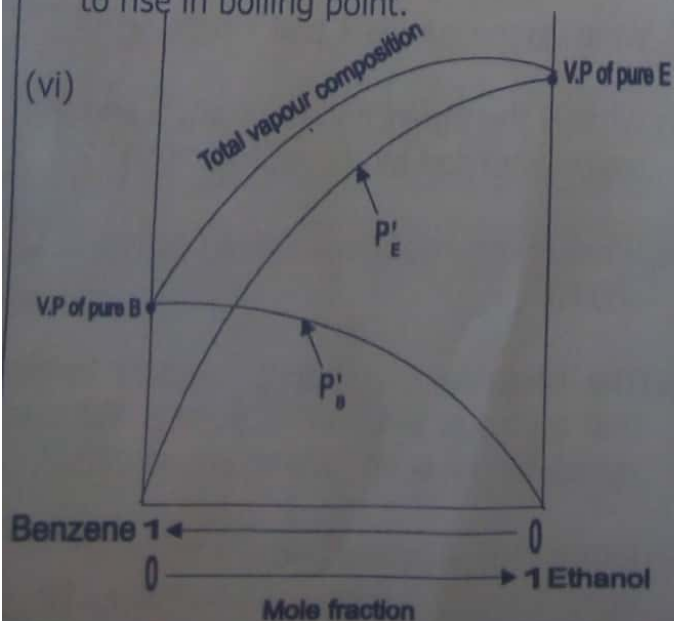


Which lowers the tendency of these molecules to escape from the solution.

- (vi) From the above boiling point composition diagram, sketch labeled diagram to illustrate the vapour pressure composition relationship for the benzene ethanol system.

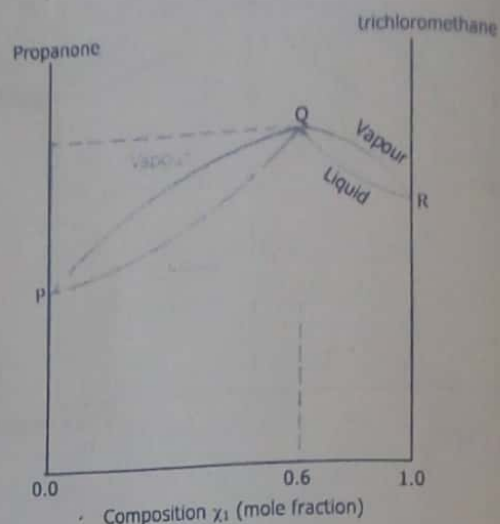
Solution

- (i) Curves X and Y represent vapour pressure and boiling temperature respectively.
- (ii) Point S refers to azeotropic point. Region between two curves to the amount of vapour collected above the liquid surface.
- (iii) The relation is when a liquid boils temperature P, give vapour corresponding to vapour pressure Q, when cooled give a liquid which boils at temperature R.
- (iv) Azeotropic solution is the liquid mixture which boils at constant temperature giving vapour above the surface of the same composition as that liquid mixture itself.
- (v) The curve appears to rise smoothly from point S to T. the rise is caused by the progressively increase in composition of ethanol solution as moving from S to T. the increase in composition of ethanol increase strength of intermolecular forces due to association of ethanol molecules by hydrogen bonding. The increase in strength of intermolecular forces results to rise in boiling point.



Qn. 106

Study the diagram below and answer the questions which follow.



- (i) What does the point P, Q and R on the diagram represent
- (ii) What would you end up with as a distillate at the end of series of distillation if you started with a solution sample of composition.

Mole fraction $x_1 = 0.72$?

Mole fraction $x_1 = 0.23$?

Solution

- (i)
- P = Boiling point of propane
Q = Azeotropic point temperature
R = Boiling point of trichloromethane.
- (ii) (a) Propanone and (b) Trichloromethane

2. COLLIGATIVE PROPERTIES OF SOLUTIONS.

(solution prepared from solvent + solid solute)

- Colligative properties of solutions:-** are properties that depend upon the concentration of solute particles, but not upon the identity of the solute.
- Colligative properties include freezing point depression, boiling point elevation,

vapour pressure lowering and osmotic pressure.

Note

Each pure solvent has its own vapour pressure, boiling point, freezing point and osmotic pressure, but all these four properties tend to change when non-volatile solutes are added to this solvent to make solution.

The size or magnitude of the change i.e. Change in temperature (Δt), change in vapour pressure (ΔP) and osmotic pressure ($\Delta \pi$) depends on the number or concentration of the solutes so added and not on their nature.

ASSUMPTION MADE ABOUT SOLUTES.

The following are assumptions made about solutes which have to be added to the solvent so as to sense the change in colligative properties.

(i) The solute should neither dissociate nor associates. Why? This is because colligative properties depends on the number of particles of solutes added now if solutes dissociate will increase in the solution the number of particles, this makes the change in colligative properties to be greater than expected from the number of particles added initially. On the other hand association reduce number of particles in the solution and hence change in colligative properties will be less than expected.

(ii) Solute should be non volatile at the boiling point of the solution. Why? This is so that solute should not contribute molecules in the vapour. All vapour collected above the solution should be due to solvent.

(ii) There should be no chemical reaction between solvent and solute.

1. LOWERING OF VAPOUR PRESSURE.

- At a given temperature solutions have less tendency of forming vapour pressure than pure solvents. Solute particles have two effects in lowering vapour pressure of the solution.

(i) Decrease the surface area for evaporation, because some of the parts of the liquid surface is covered by the solute particles, therefore comparatively less surface area is available for evaporation. Then solvent molecules which are about to escape from the solution bounce on the solute particles present in the surface and drop back into the solution. Hence the vapour pressure is lowered.

(ii) Increase in inter-molecular forces. Solute particles occupy interstitial spaces left in between solvent molecules and hence the distance between particles and solvent molecules becomes small. The solution becomes concentrated. Decrease in distance has effect of increase in intermolecular forces.

- The relationship between the vapour pressure lowered (ΔP) and the amount of solute added is given by Raoult's law

- Raoult's law states that " The relative lowering in vapour pressure is equal to the mole fraction of the solute present in the solution.

Mathematically

$$\frac{P_o - P_{soln}}{P_o} = \frac{n_s}{n_s + n_o}$$

Or

$$\frac{\Delta P}{P_o} = \frac{n_s}{n_s + n_o} \dots\dots\dots(i)$$

Where

P_o = Vapour pressure of the solvent

P_{soln} = vapour pressure of the solution.

ΔP = Change in vapour pressure i.e. ($P_o - P_{soln}$)

n_s = Number of moles of solute

n_o = Number of moles of solvent.

Recall expression (i) above.

i.e.
$$\frac{\Delta P}{P_o} = \frac{n_s}{n_s + n_o}$$

But, number of moles = $\frac{\text{mass (weight)}}{\text{Molar mass}}$

Then,

$$\frac{\Delta P}{P_o} = \frac{W_s/Mr_s}{W_o/Mr_o + W_s/Mr_s} \quad (\text{for concentrated solution})$$

- But for dilute solution where the amount of solvent is larger compared to amount of solute, $n_s + n_o \approx n_o$

Thus,

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \div \frac{w_o}{Mr_o}$$

Or

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

Where,

w_s = weight of the solute

w_o = weight of the solvent

Mr_s = Molar mass of solute

Mr_o = molar mass of solvent.

Note.

If the solution is dilute, then Raoult's law can be used to find the P_{soln} , P_o or ΔP as follows

$$P_{\text{soln}} = \chi_o \cdot P_o$$

The reduction in the vapour pressure of solvent (ΔP) is given as,

$$\Delta P = P_o - P_{\text{soln}}$$

or

$$\Delta P = P_o - P_o \cdot \chi_o$$

$$\Delta P = P_o(1 - \chi_o)$$

Knowing that $\chi_s = 1 - \chi_o$, thus,

$$\Delta P = P_o \cdot \chi_s$$

Qn. 107

Calculate the vapour pressure of a solution made by dissolving 218g of glucose ($C_6H_{12}O_6$) in 460ml of water at 30°C. What is the vapour pressure lowered? The vapour pressure of pure water at 30°C is 31.82mmHg.

Solution

From,

$$P_{\text{soln}} = \chi_o \cdot P_o$$

1st case:

Calculate the number of moles of glucose and water.

$$n_o = \frac{460g}{18g\text{mol}^{-1}} = 25.6\text{moles}$$

$$n_s = \frac{218g}{180g\text{mol}^{-1}} = 1.21\text{moles}$$

The mole fraction of water is thus.

$$\chi_o = \frac{25.6}{26.81} = 0.955$$

$$\chi_s = 0.045$$

Since the vapour pressure of water at 30°C is 31.82mmHg thus the vapour pressure of glucose solution is,

$$P_{\text{soln}} = \chi_o P_o$$

$$P_{\text{soln}} = 0.955 \times 31.82\text{mmHg}$$

$$P_{\text{soln}} = 30.4\text{mmHg}$$

Finally the vapour pressure lowering is $(31.82 - 30.4) \text{ mmHg} = 1.4\text{mmHg}$

Alternative

Data

$$W_s = 218g$$

$$V_o = 460\text{ml}$$

$$P_o = 31.82\text{mmHg}$$

From

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{\Delta P}{31.82} = \frac{218}{180} \times \frac{18}{460}$$

$$\Delta P = 1.51 \text{ mmHg}$$

Then, the vapour pressure lowered is 1.51 mmHg. And vapour pressure of the solution will be $31.82 - 1.51 = 30.3 \text{ mmHg}$.

Qn. 108

A solution was prepared by adding 20g of urea to 125g water at 25°C, a temperature at which pure water has a vapour pressure of 23.76 torr. The observed vapour pressure of the solution was found to be 22.67 torr. Calculate the molar mass of urea.

Solution

From,

$$P_{\text{soln}} = \chi_o \cdot P_o$$

Or

$$\chi_o = \frac{P_{\text{soln}}}{P_o} = \frac{22.67 \text{ torr}}{23.76 \text{ torr}} = 0.9541$$

Then mole fraction of water in the solution is thus 0.9541.

However, we are interested in the urea. To find its molar mass, we must find the number of moles represented by 20g.

From,

$$\chi_o = \frac{n_o}{n_o + n_s} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{urea}}}$$

Then,

$$n_o = \frac{125}{18} = 6.94 \text{ moles}$$

Then

$$\chi_o = \frac{6.94}{6.94 + n_s}$$

$$\frac{0.9541}{1} = \frac{6.94}{6.94 + n_s}$$

$$6.63 + 0.9541n_s = 6.94$$

$$0.9541n_s = 6.94 - 6.63$$

$$\frac{0.9541n_s}{0.9541} = \frac{0.31}{0.9541}$$

$$n_s = 0.335 \text{ moles.}$$

But

$$n_s = \frac{\text{mass}}{M_r}$$

$$M_r = \frac{\text{mass}}{n_s} = \frac{20}{0.335} = 60 \text{ g mol}^{-1}$$

Alternative,

Data

$$w_s = 20 \text{ g}$$

$$w_o = 125 \text{ g}$$

$$P_o = 23.76 \text{ torr}$$

$$P_{\text{soln}} = 22.67 \text{ torr}$$

From

$$\frac{\Delta P}{P_o} = \frac{w_s}{M_r_s} \times \frac{M_r_o}{w_o}$$

$$\frac{1.09}{23.76} = \frac{20}{M_r_s} \times \frac{18}{125}$$

$$M_r_s = \frac{23.76 \times 20 \times 18}{1.09 \times 125}$$

$$M_r_s = 62.78 \text{ g mol}^{-1}$$

Qn. 109

Calculate the expected vapour pressure of 25°C for a solution prepared by dissolving 158g of common table sugar (sucrose) in 643.5 cm³ water. At 25°C the density of water is 0.997 g/cm³ and the vapour pressure is 23.76 torr.

Solution

Data

$$M_s = 158 \text{ g}$$

$$V_o = 643.5 \text{ cm}^3$$

$$d_o = 0.997 \text{ g/cm}^3$$

$$P_o = 23.76 \text{ torr.}$$

Find number of moles of sucrose (n_s)

$$n_s = \frac{\text{mass}}{M_r} = \frac{158 \text{ g}}{342.3 \text{ g mol}^{-1}} = 0.4616 \text{ moles}$$

Convert volume of water to mass

If

$$0.997 \text{ g} \rightarrow 1 \text{ cm}^3$$

$$\times \leftarrow 643.5 \text{ cm}^3$$

$$m_o = 641.6g \text{ H}_2\text{O}$$

Then,

$$n_o = \frac{m_o}{Mr_o} = \frac{641.6g}{18g\text{mol}^{-1}}$$

$$n_o = 35.64\text{mol H}_2\text{O}$$

Also

$$\chi_o = \frac{n_o}{n_o + n_s}$$

$$\chi_o = \frac{35.64}{35.64 + 0.4616}$$

$$\chi_o = 0.9872.$$

Then

$$P_{\text{soln}} = P_o \cdot \chi_o$$

$$P_{\text{soln}} = (23.76\text{torr})(0.9872)$$

$$P_{\text{soln}} = 23.46\text{torr.}$$

Alternative,

Data

$$w_s = 158g$$

$$w_o = 641.6g \text{ (by conversion from density)}$$

$$P_o = 23.76\text{torr}$$

From,

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{\Delta P}{23.76} = \frac{158}{342.3} \times \frac{18}{641.6}$$

$$\Delta P = \frac{23.76 \times 158 \times 18}{342.3 \times 641.6}$$

$$\Delta P = 0.31\text{torr}$$

Then,

$$P_{\text{soln}} = P_{\text{solvent}} - \Delta P$$

$$P_{\text{soln}} = (23.76 - 0.31) \text{ torr.}$$

$$P_{\text{soln}} = 23.45\text{torr.}$$

Qn. 110

Predict the vapour pressure of a solution prepared by mixing 35g solid Na_2SO_4 (molar mass = $142g\text{mol}^{-1}$) with 175g water at 25°C . The vapour pressure of pure water at 25°C is 23.76torr.

Solution

Data

$$m_s = 35g$$

$$m_o = 175g$$

$$P_o = 23.76\text{torr.}$$

Find the mole fraction of water, but find number of moles of solid and water first.

Then,

$$n_o = \frac{m_o}{Mr_o} = \frac{175g}{18g\text{mol}^{-1}} = 9.72g\text{moles}$$

Also,

$$n_s(\text{Na}_2\text{SO}_4) = \frac{35g}{142g\text{mol}^{-1}} = 0.246\text{moles}$$

It is essential to recognize that when 1mol of Na_2SO_4 dissolves, it produces 2mol of Na^+ and 1mol SO_4^{2-} ions. Thus the number of solute particles present in this solution is,
 $= 3 \times (0.245)\text{moles}$
 $= 0.738\text{moles}$

Then,

$$\chi_o = \frac{n_o}{n_o + n_s} = \frac{9.72}{(9.72 + 0.738)}$$

$$\chi_o = 0.929$$

Now we can use Raoult's law to vapour pressure.

i.e.

$$P_{\text{soln}} = \chi_o \cdot P_o$$

$$P_{\text{soln}} = 0.929 \times 23.76 \text{ torr}$$

$$P_{\text{soln}} = 22.1\text{torr.}$$

Alternative,

Data

$$w_s = 35g$$

$$w_o = 175g$$

$$P_o = 23.76\text{torr}$$

$$n_s = 0.246 \text{ moles}$$

$$n_o = 9.72 \text{ moles}$$

It must be noted that when 1mol of Na_2SO_4 dissociates it produces 2 moles of Na^+ and 1mol of SO_4^{2-} . Thus the number of solute particles present in this solution will be $3 \times (0.246) \text{ moles}$

i.e.

$$0.738 \text{ moles}$$

Then, from

$$\frac{\Delta P}{P_o} = \frac{n_s}{n_o}$$

$$\frac{\Delta P}{23.76} = \frac{0.738}{9.72}$$

$$\Delta P = 1.8 \text{ torr}$$

Thus, vapour pressure of the solution is
 $(23.76 - 1.8) \text{ torr}$
 $= 21.96 \text{ torr}$.

Qn. 111

A solution is prepared by mixing 50g glucose with 600g water. What is the vapour pressure of this solution at 25°C ? At 25°C the vapour pressure of water is 23.8torr.

Solution

Data

$$m_s = 50 \text{ g}$$

$$m_o = 600 \text{ g}$$

$$P_o = 23.8 \text{ torr}$$

1st Case: Find the mole fraction of water.

From

$$\chi_o = \frac{n_o}{n_o + n_s}$$

But

$$n_o = \frac{600 \text{ g}}{18 \text{ mol}^{-1}} = 33.33 \text{ moles}$$

$$n_s = \frac{50 \text{ g}}{180 \text{ g mol}^{-1}} = 0.278 \text{ moles}$$

Then,

$$\chi_o = \frac{33.33}{33.33 + 0.278}$$

$$\chi_o = 0.992$$

2nd Case: From Raoult's law find V. pressure of solution

$$P_{\text{soln}} = \chi_o \cdot P_o$$

$$P_{\text{soln}} = 0.992 \times 23.8 \text{ torr}$$

$$= 23.6 \text{ torr}$$

Alternative,

Data

$$w_s = 50 \text{ g}$$

$$w_o = 600 \text{ g}$$

$$P_o = 23.8 \text{ torr}$$

From

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{\Delta P}{23.8} = \frac{50}{180} \times \frac{18}{600}$$

$$\Delta P = \frac{23.8 \times 50 \times 18}{180 \times 600}$$

$$\Delta P = 0.2 \text{ torr}$$

Then

$$P_{\text{soln}} = P_o - \Delta P$$

$$= (23.8 - 0.2) \text{ torr}$$

$$= 23.6 \text{ torr}$$

Qn. 112

How many grams of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) must be added to 552g of water to give a solution with a vapour pressure 2mmHg less than that of pure water at 20°C ? the vapour pressure of water at 20°C is 17.5mmHg.

Solution

Data

$$Mr_s = 342.3 \text{ g mol}^{-1}$$

$$Mr_o = 18 \text{ g mol}^{-1}$$

$$m_o = 552 \text{ g}$$

$$\Delta P = 2 \text{ mmHg}$$

$$P_o = 17.5 \text{ mmHg}$$

1st Case:

Find the mole fraction of water

i.e. But, $n_o = \frac{m_o}{Mr}$

$$n_o = \frac{552g}{18gmol^{-1}} = 30.67 \text{ moles}$$

Also,

$$\chi_o = \frac{n_o}{n_o + n_s}$$

$$\chi_o = \frac{30.67}{30.67 + n_s} \dots\dots\dots(i)$$

But

$$\chi_o = \frac{P_{soln}}{P_o}$$

$$\chi_o = \frac{15.5}{17.5} = 0.886$$

2nd Case: Find n_s substituting $\chi_o = 0.886$ in equation (i) above

i.e.

$$0.886 = \frac{30.67}{30.67 + n_s}$$

$$27.174 + 0.886n_s = 30.67$$

$$0.886n_s = 30.67 - 27.174$$

$$\frac{0.886n_s}{0.886} = \frac{3.496}{0.886}$$

$$n_s = 3.946 \text{ moles}$$

But $n = \frac{m}{Mr}$

$$\text{Mass} = n_s \times Mr_s$$

$$\text{Mass} = 3.946 \times 342.3 \text{ moles} \times gmol^{-1}$$

$$\text{Mass} = \underline{1351g}$$

Alternative,

Data

$$Mr_s = 342.3gmol^{-1}$$

$$w_o = 552g$$

$$\Delta P = 2mmHg$$

$$P_o = 17.5mmHg$$

From

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{2}{17.5} = \frac{w_s}{342.3} \times \frac{18}{552}$$

$$w_s = \frac{2 \times 342.3 \times 552}{17.5 \times 18}$$

$$w_s = \underline{1199.79}$$

Note

In determining the vapour pressure of the solution, vapour pressure of the pure solvent and vapour pressure lowered it seems that any of the two formula gave almost equal results.

But on determination of mass of the substance or molar mass gave quite large difference. So it is preferred to use the equation.

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

In calculating the mass or molar mass of the substance, and each of the formula to find P_{soln} , P_o or ΔP .

Qn. 113

The vapour pressure of pure benzene at a certain temperature is 0.85atm. 0.5g non electrolyte and non-volatile solid is added to 39g of benzene. The vapour pressure of this solution is found to be 0.845atm. Calculate the molecular mass of the substance.

Solution

Data

$$P_o = 0.8atm$$

$$P_{soln} = 0.845atm$$

$$w_s = 0.5g$$

$$w_o = 39g$$

$$Mr_o = 78gmol^{-1}$$

From,

$$\frac{P_0 - P_{\text{soln}}}{P_0} = \frac{w_s}{Mr_s} \times \frac{Mr_0}{w_0}$$

Then

$$\frac{0.85 - 0.845}{0.85} = \frac{0.5}{Mr_s} \times \frac{78}{39}$$

$$Mr = \frac{0.5 \times 78}{0.00588 \times 39} \quad Mr = 170 \text{ g mol}^{-1}$$

Hence the molar mass of the substance is 170 g mol^{-1}

Qn. 114

An aqueous solution of glucose is made by dissolving 10g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in 90g of water at 303K. If the vapour pressure of pure water at 303K be 32.8mmHg, what would be the vapour pressure of the solution?

Solution

Data

$$w_s = 10\text{g}$$

$$w_0 = 90\text{g}$$

$$P_0 = 32.8$$

$$Mr_s = 180 \text{ g mol}^{-1}$$

$$Mr_0 = 18 \text{ g mol}^{-1}$$

From,

$$\frac{\Delta P}{P_0} = \frac{w_s}{Mr_s} \times \frac{Mr_0}{w_0}$$

Then

$$\frac{\Delta P}{32.8} = \frac{10}{180} \times \frac{18}{90}$$

$$\frac{\Delta P}{32.8} = \frac{180}{16,200}$$

$$\Delta P = \frac{0.0111}{32.8}$$

$$\Delta P = 0.0111 \times 32.8$$

$$\Delta P = 0.364 \text{ mmHg.}$$

$$P_{\text{soln}} = 32.8 - 0.364$$

$$P_{\text{soln}} = 32.44 \text{ mmHg}$$

Hence the vapour pressure of solution is 32.44mmHg.

Qn. 115

10.6g of non-volatile, non-dissociating solute Q is dissolved in 90g of water. If the vapour pressure of the solution is 0.186atm at 60C. Calculate the approximate molecular weight (mass) of the solute. The vapour pressure of water at 60C is 0.1966atm.

Solution

Data:

$$w_s = 10.6\text{g}$$

$$w_0 = 90\text{g}$$

$$P_{\text{soln}} = 0.186 \text{ atm}$$

$$P_0 = 0.1966 \text{ atm}$$

$$Mr_0 = 18 \text{ g mol}^{-1}$$

From

$$\frac{\Delta P}{P_0} = \frac{w_s}{Mr_s} \times \frac{Mr_0}{w_0}$$

$$\frac{0.1966 - 0.1867}{0.1966} = \frac{10.6}{Mr_s} \times \frac{18}{90}$$

$$\frac{0.0099}{0.1966} = \frac{10.6}{Mr_s} \times \frac{18}{90}$$

$$Mr_s = \frac{0.1966 \times 10.6 \times 18}{0.0099 \times 90}$$

$$Mr_s = 42 \text{ g mol}^{-1}$$

Hence the approximate molecular weight is 42 g mol^{-1} .

Qn. 116

The vapour pressure of 95% aqueous solution of a non-volatile organic substance at 373K is 745mmHg. At the same temperature vapour pressure of pure solvent is 760mmHg. Calculate the molar mass of the substance.

Solution

Note; A 5% aqueous solution of non volatile substance means that 5g is dissolved in 95g of solvent.

Data

$$\begin{aligned}w_s &= 5\text{g} \\w_o &= 95\text{g} \\P_{\text{soln}} &= 745\text{mmHg} \\P_o &= 760\text{mmHg} \\Mr_o &= 18\text{gml}^{-1}\end{aligned}$$

From

$$\frac{P_o - P_{\text{soln}}}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{15}{760} = \frac{5}{Mr_s} \times \frac{18}{95}$$

$$Mr_s = \frac{760 \times 5 \times 18}{15 \times 95}$$

$$Mr_s = 48\text{gmol}^{-1}$$

Hence the molar mass of the substance is 48gmol^{-1}

Qn. 117

Calculate the relative molar mass of a non volatile solute 5g of which have been dissolved in 100g of ether if vapour pressure of solution and pure ether are 412mmHg and 440mmHg respectively at 293K (assume very dilute solution) Molar mass of ether is 75gmol^{-1} .

Solution

Data

$$\begin{aligned}w_s &= 5\text{g} \\w_o &= 100\text{g} \\P_{\text{soln}} &= 412\text{mmHg} \\P_o &= 440\text{mmHg} \\Mr_o &= 74\text{gmol}^{-1}\end{aligned}$$

From,

$$\frac{P_o - P_{\text{soln}}}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{28}{440} = \frac{5}{Mr_s} \times \frac{74}{100}$$

$$Mr_s = \frac{440 \times 5 \times 74}{28 \times 100}$$

$$Mr_s = 58.14\text{gmol}^{-1}$$

Hence the relative molar mass is 58.14

Qn. 118

The vapour pressure of water at 50°C was 920mmHg. When 19.1g of an organic substance K were dissolved in 100g of water, the water vapour pressure dropped by 50mmHg. Calculate the relative molecular mass of substance K.

Solution.

Data

$$\begin{aligned}P_o &= 920\text{mmHg} \\w_s &= 19.1\text{g} \\w_o &= 100\text{g} \\ \Delta P &= 50\text{mmHg} \\Mr_o &= 18\text{gmol}^{-1}\end{aligned}$$

From,

$$\frac{\Delta P}{P_o} = \frac{w_s}{Mr_s} \times \frac{Mr_o}{w_o}$$

$$\frac{50}{920} = \frac{19.1}{Mr_s} \times \frac{18}{100}$$

$$Mr_s = \frac{920 \times 19.1 \times 18}{50 \times 100}$$

$$Mr_s = 63.26\text{gmol}^{-1}$$

But relative molecular mass is 63.26

Qn. 119

The vapour pressure of ethoxyethane ($\text{C}_4\text{H}_{10}\text{O}$) at a certain temperature was 66430N/m^2 . When 3.6g of an organic acid were dissolved in 67g of ethoxyethane the

vapour pressure fell to 629600N/m². Calculate the relative molar mass of the organic acid (Assume the solution to be very dilute)

Solution

Data

$$\begin{aligned} P_o &= 664300 \text{ N/m}^2 \\ P_{\text{soln}} &= 629600 \text{ N/m}^2 \\ w_s &= 3.6 \text{ g} \\ w_o &= 67 \text{ g} \\ M_{r_o} &= 74 \text{ g mol}^{-1} \end{aligned}$$

From

$$\frac{P_o - P_{\text{soln}}}{P_o} = \frac{w_s}{M_{r_s}} \times \frac{M_{r_o}}{w_o}$$

$$\frac{34700}{664300} = \frac{3.6}{M_{r_s}} \times \frac{74}{67}$$

$$M_{r_s} = 76 \text{ g mol}^{-1}$$

Then the relative molar mass of the organic acid is 76.

Qn. 120

A solution containing 30g of a non volatile solute in 90g of water has a vapour pressure of 2.8Kpa at 298K. Further 18g of water is then added to solution, the new vapour pressure becomes 2.9Kpa at 298K. Calculate
(i) Vapour pressure of water at 298K
(ii) Molar mass of solute.

Solution

Data

1st case

$$\begin{aligned} w_s &= 30 \text{ g} \\ w_o &= 90 \text{ g} \\ P_{\text{soln}} &= 2.8 \text{ Kpa} \end{aligned}$$

2nd case

$$\begin{aligned} w_s &= 30 \text{ g} \\ w_o &= 108 \text{ g} \\ P_{\text{soln}} &= 2.9 \text{ Kpa} \end{aligned}$$

From 1st case

$$\frac{P_o - P_{\text{soln}}}{P_o} = \frac{w_s}{M_{r_s}} \times \frac{M_{r_o}}{w_o}$$

$$\frac{P_o - 2.8}{P_o} = \frac{30}{M_{r_s}} \times \frac{18}{90}$$

$$\frac{P_o - 2.8}{P_o} = \frac{6}{M_{r_s}} \dots\dots\dots (i)$$

From 2nd case

$$\frac{\Delta P}{P_o} = \frac{w_s}{M_{r_s}} \times \frac{M_{r_o}}{w_o}$$

$$\frac{P_o - 2.9}{P_o} = \frac{30}{M_{r_s}} \times \frac{18}{108}$$

$$\frac{P_o - 2.9}{P_o} = \frac{5}{M_{r_s}} \dots\dots\dots (ii)$$

Taking ratio of an eqn (i) and (ii) we get

$$\frac{P_o - 2.8}{P_o - 2.9} = \frac{6}{5}$$

$$\frac{P_o - 2.8}{P_o - 2.9} = 1.2$$

$$P_o - 2.8 = 1.2P_o - 3.48$$

$$2.8 + 3.48 = 1.2P_o - P_o$$

$$\frac{0.68}{0.2} = \frac{0.2P_o}{0.2}$$

$$P_o = 3.4 \text{ Kpa}$$

Then vapour pressure of water at 298K is 3.4Kpa.

(i) Required molar mass of solute

From eqn (i)

$$\frac{P_o - 2.8}{P_o} = \frac{6}{M_{r_s}}$$

$$\frac{3.4 - 2.8}{3.4} = \frac{6}{M_{r_s}}$$

$$\frac{0.6}{3.4} = \frac{6}{M_{r_s}}$$

Hence molar mass of solute is 34g mol^{-1} .

Alternatively

From eqn (ii)

$$\frac{P_0 - 2.1}{P_0} = \frac{5}{M_{r_s}}$$

$$\frac{3.4 - 2.9}{3.4} = \frac{5}{M_{r_s}}$$

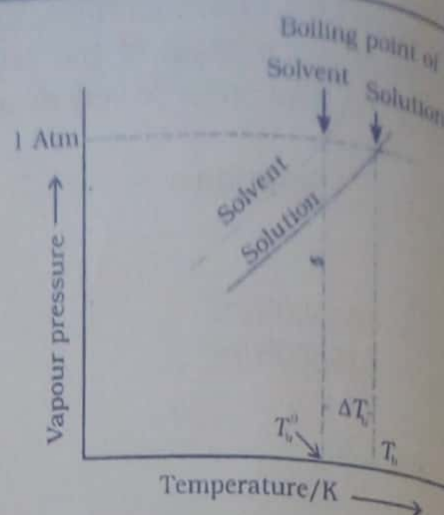
$$\frac{0.5}{3.4} = \frac{5}{M_{r_s}}$$

$$M_{r_s} = 34\text{g mol}^{-1}$$

2. BOILING POINT ELEVATION AND FREEZING POINT DEPRESSION.

(i) BOILING POINT ELEVATION.

- Normally the vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure.
- We also know that vapour pressure of the solvent decreases in the presence of non-volatile solute. Hence, a higher temperature must be reached before the solution boils that is before its vapour pressure becomes equal to the atmospheric pressure.
- From these points of view it appears that a solution boils at higher temperature than boiling point of the pure solvent. The elevation of boiling point also depends on the number of solute molecules rather than their nature.
- The increase in the boiling point, $\Delta T_b = \text{Bp. of solution} - \text{Bp. of solvent}$ is known as Elevation of boiling point.



- Experiment have shown that for dilute solutions the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution.

i.e.

$$\Delta T_b \propto m$$

Or

$$\Delta T_b = K_b \cdot m \dots\dots\dots(i)$$

- Here m (molality) is the number of moles of solute dissolved in 1000g (1kg) of the solvent.
- K_b is the proportionality constant called **Boiling point elevation constant** or **molal elevation constant** (**Ebullioscopic constant**).

EBULLIOSCOPIC CONSTANT:-

- Is the boiling temperature elevation constant when one mole of the solute is dissolved in one kilogram of the solvent. The unit of K_b is K kg mol^{-1} .
- If w_s is the weight of the solute (in gram) of molar mass M_r dissolved in weight of the solvent (w_o) in gram, then molality m of the solution is given by the expression.

$$m = \frac{w_s / M_r}{w_o / 1000}$$

$$m = \frac{w_s \times 1000}{M_r \times w_o}$$

- Substituting the value of molality in equation (i) above we get

$$\Delta T_b = \frac{K_b \times w_s \times 1000}{M_r \times w_o}$$

$$M_r = \frac{K_b \times w_s \times 1000}{\Delta T_b \times w_o}$$

i) FREEZING POINT DEPRESSION.

The lowering of vapour pressure of a solution causes a lowering of freezing point compared to that of pure solvent.

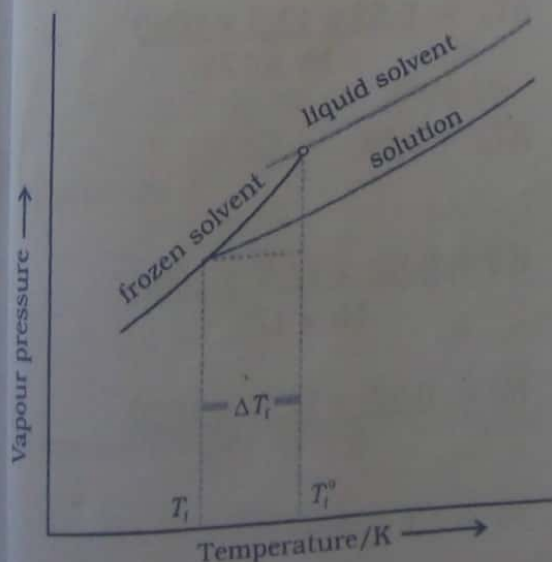
We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid state is equal to its vapour pressure in the solid phase.

A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent.

According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

The decrease in freezing point,

$\Delta T_f = \text{Fp. of solvent} - \text{Fp of solution}$
known as Depression in freezing point.



Similar to elevation of boiling point, depression of freezing point (ΔT_f) for dilute solution (ideal solution) is directly proportional to molality, m of the solution. Thus

$$\Delta T_f \propto m$$

Or

$$\Delta T_f = K_f \cdot m \dots\dots\dots (i)$$

- The proportionality constant, K_f which depends on the nature of the solvent is known as **freezing point depression constant** or **molal depression constant (Cryoscopic constant)**

CRYOSCOPIC CONSTANT:-

- Is the freezing point depression constant when one mole of the solute is dissolved in 1000g (1kg) of the solvent. The unit of K_f is Kkgmol^{-1} .
- If w_s is the gram of the solute having molar mass M_r present in w_o gram of solvent, produces the depression in freezing point ΔT_f of the solvent, then molality of the solute is given as,

$$m = \frac{w_s / M_r}{w_o / 100}$$

- Substituting this value of molality in equation (i) above we get.

$$\Delta T_f = \frac{K_f \times w_s \times 1000}{M_r \times w_o}$$

Or

$$M_r = \frac{K_f \times w_s \times 1000}{\Delta T_f \times w_o}$$

Qn. 121

Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is a common automobile antifreeze. It is water soluble and fairly non volatile (b.p 197°C). Calculate (a) the freezing point and (b) the boiling point of a solution containing 685g of ethylene glycol in 207g of water. K_b and K_f for water are 0.52°C/m and 1.86°C/m , respectively.

Solution

Data

$$w_s = 685g$$

$$w_o = 2075g$$

$$Mr_s = 62.1g$$

From,

$$\Delta T_f = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

$$\Delta T_f = \frac{1.86 \times 685 \times 1000}{62.1 \times 2075}$$

$$T_f = 9.89^\circ C$$

Thus the freezing point of the solution is $0 - 9.89^\circ C = -9.89^\circ C$ or $263.11K$.

Also

$$\Delta T_b = \frac{K_b \times w_s \times 1000}{Mr \times w_o}$$

$$\Delta T_b = \frac{0.52 \times 685 \times 1000}{62.1 \times 2075}$$

$$\Delta T_b = 2.8^\circ C$$

Thus boiling point of solution,
= Bp. of solvent + ΔT_b
= $100^\circ C + 2.8^\circ C$
= $102.8^\circ C$ or $375.8K$

Qn. 122

Quinine was the first drug widely used to treat malaria, and it remains the treatment of choice for severe cases. A solution prepared by dissolving 10g of quinine in 50ml of ethanol has a freezing point $1.55^\circ C$ below that of pure ethanol. Determine the molar mass of quinine. (the density of ethanol is $0.789g/ml$). Assume that quinine is non electrolyte. K_f for ethanol is $1.99^\circ C/m$.

Solution

1st case

Using the density of ethanol to determine its mass from 50ml.

i.e.

$$\begin{array}{l} 0.789g \longrightarrow 1ml \\ x g \longleftarrow 50ml \end{array}$$

$$m_{eth} = \frac{0.789g \times 50ml}{1ml} = 39.45g$$

From,

$$\Delta T_f = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

$$Mr = \frac{K_f \times w_s \times 1000}{\Delta T_f \times w_o}$$

$$Mr = \frac{1.99 \times 10 \times 1000}{1.55 \times 39.5}$$

$$Mr = 325g/mol$$

Then molar mass of quinine is $325g/mol$

Qn. 123

A solution containing 12.5g of a non-electrolyte, none volatile solute in 175g of water gave a boiling point elevation of $0.7K$. Calculate the molar mass of the substance (K_b (H_2O) is $0.52K/gmol^{-1}$).

Solution

Data

$$w_s = 12.5g$$

$$w_o = 175g$$

$$\Delta T_b = 0.7K$$

$$K_b(H_2O) = 0.52K/gmol^{-1}$$

From,

$$\Delta T_b = \frac{K_b \times w_s \times 1000}{Mr \times w_o}$$

$$\Delta T_b = \frac{0.52 \times 12.5 \times 1000}{Mr \times 175}$$

But $\Delta T_b = 0.7K$.

Then,

$$0.7 = \frac{0.52 \times 12.5 \times 1000}{Mr \times 175}$$

$$Mr = \frac{0.52 \times 12.5 \times 1000}{0.7 \times 175}$$

$$Mr = 53.1g/mol$$

Qn. 124

pheromones are compounds secreted by the female of many insect species to attract males. One of these compounds contains 80.78% C, 13.56% H and 5.66% O. A solution of 1g of this pheromones in 8.5g of benzene freezes at 3.37°C. What are the molecular formula and molar mass of the compounds? The normal freezing point of pure benzene is 5.5°C and its $K_f = 5.12 \text{ K kg mol}^{-1}$.

Solution

Data

$$\begin{aligned} w_s &= 1\text{g} \\ w_o &= 8.5\text{g} \\ \Delta T_f &= 2.13^\circ\text{C} \\ K_f &= 5.12 \text{ K kg mol}^{-1} \end{aligned}$$

1st Case: Find the molar mass of the pheromones

From,

$$\Delta T_f = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

$$Mr = \frac{K_f \times w_s \times 1000}{\Delta T_f \times w_o}$$

$$Mr = \frac{5.12 \times 1 \times 1000}{2.13 \times 8.5}$$

$$Mr = 282.8 \text{ g mol}^{-1}$$

2nd Case: Find the empirical formula of pheromones.

i.e.

C	H	O
80.78	13.56	5.66
12	1	16
<u>6.73</u>	<u>13.56</u>	<u>0.354</u>
0.354	0.354	0.354
19	38	1

Then empirical formula is $\text{C}_{19}\text{H}_{38}\text{O}$.

3rd Case: Find the molecular formula.

From,

$$\begin{aligned} (EF)_n &= Mr. \\ (\text{C}_{19}\text{H}_{38}\text{O})_n &= 282.8 \end{aligned}$$

$$228n + 38n + 16n = 282.8$$

$$\frac{282.13n}{282.13} = \frac{282.8}{282.13}$$

$$n = 1$$

Then molecular formula of pheromone is $\text{C}_{19}\text{H}_{38}\text{O}$.

Qn. 125

The freezing point of pure nitrobenzene is 278.8K when 2.5g of unknown substance is dissolved in 100g of nitrobenzene, the freezing point of the solution is found to be 276.8K. If the freezing point depression constant of nitrobenzene is 8K Kg/mol, what is the molar mass of unknown substance?

Solution

Data

$$\begin{aligned} w_s &= 2.5\text{g} \\ w_o &= 100\text{g} \\ \Delta t &= 2\text{K} \\ K_f &= 8\text{K Kg/mol} \end{aligned}$$

Required: Molar mass

Recall

$$\Delta t = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

$$2 = \frac{8 \times 2.5 \times 1000}{Mr \times 100}$$

$$Mr = 100 \text{ g mol}^{-1}$$

Hence the molar mass of unknown substance is 100 g mol^{-1} .

Qn. 126

0.9g of non-electrolyte was dissolved in 87.9g of benzene. This raised the boiling point of benzene by 0.25°C if the molecular mass of the non-electrolyte is 103 g mol^{-1} . Calculate the molar elevation constant of benzene.

Data

$$\begin{aligned}w_s &= 0.9\text{g} \\w_o &= 87.9\text{g} \\\Delta t &= 0.25^\circ\text{C} \\M_r &= 103\text{gmol}^{-1} \\K_b &= ?\end{aligned}$$

Solution

From

$$\Delta t = \frac{K_b \times w_s \times 1000}{M_r \times w_o}$$

$$0.25 = \frac{K_b \times 0.9 \times 100}{103 \times 87.9}$$

$$K_b = \frac{0.25 \times 103 \times 87.9}{0.9 \times 1000}$$

$$K_b = 2.5^\circ\text{C/m}$$

Qn. 127

45g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is mixed with 600g of water. Calculate the freezing point depression and freezing point of the solution ($K_f \text{H}_2\text{O} = 1.86^\circ\text{C/m}$)

Solution

Data

$$\begin{aligned}w_s &= 45\text{g} \\w_o &= 600\text{g} \\K_f &= 1.86^\circ\text{C/m}\end{aligned}$$

(i) Required: Freezing point depression

From

$$\Delta t = \frac{K_f \times w_s \times 1000}{M_r \times w_o}$$

$$\Delta t = \frac{1.86 \times 45 \times 1000}{62 \times 600}$$

$$\Delta t = 2.25^\circ\text{C}$$

Then freezing point depression is 2.25°C

(ii) **Required:** freezing point of the solution
i.e. Fpt of the solution = Fpt of solvent - Δt

$$\text{Fpt of soln} = 0^\circ\text{C} - 2.25^\circ\text{C}$$

$$\text{Fpt of soln} = -2.25^\circ\text{C}$$

Then the freezing point of the solution

is 2.25°C or 270.75K .

Qn. 128

A 5% solution (by mass) of cane sugar in water has freezing point of 271K . Calculate the freezing point of a 5% glucose in water if freezing point of pure water is 273.15K .

Solution

A 5% solution by mass of cane sugar means 5g is dissolved in 95g of water.

Data

$$\begin{aligned}w_s &= 5\text{g} \\w_o &= 95\text{g} \\\Delta t &= 2.15\text{K} \\M_{r \text{ cane sugar}} &= 342\text{gmol}^{-1}\end{aligned}$$

From,

$$\Delta t = \frac{K_f \times w_s \times 1000}{M_r \times w_o}$$

$$K_f = \frac{\Delta t \times M_r \times w_o}{w_s \times 1000}$$

$$K_f = \frac{2.15 \times 342 \times 95}{5 \times 1000}$$

$$K_f = 14\text{K/m}$$

For glucose

$$\Delta t = \frac{K_f \times w_s \times 1000}{M_r \times w_o}$$

$$\Delta t = \frac{14 \times 5 \times 1000}{180 \times 95}$$

$$\Delta t = 4.1\text{K}$$

Then freezing point of a soln.
= Fpt of solvent - Δt
= $273.15 - 4.1$
= 269.05K

Qn. 129

Calculate the freezing point of a solution containing 0.52g of glucose dissolved in 80.2g of water. For water $K_f = 1.86^\circ\text{C/m}$

Solution

Data

$$\begin{aligned}w_s &= 0.52\text{g} \\w_o &= 80.2\text{g} \\K_f &= 1.86^\circ\text{C/m} \\Mr &= 190\text{g mol}^{-1}\end{aligned}$$

From

$$\Delta t = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

$$\Delta t = \frac{1.86 \times 0.52 \times 1000}{180 \times 80.2}$$

$$\Delta t = 0.07^\circ\text{C} \text{ or } 0.07\text{K}$$

$$\begin{aligned}\text{Freezing point of solution} &= \text{Fpt of solvent} - \Delta t \\&= 272 - 0.07\text{K} \\&= 272.93\text{K}\end{aligned}$$

Qn. 130

Through an experiment, 1.35g of solute TB were dissolved in 72.3cm³ of water and the solution was found to boil at 100.162°C at 1atm, if the boiling point constant for 100g of water is 5.2K. Calculate the molecular weight of solute TB.

Solution

Data

$$\begin{aligned}w_s &= 1.35\text{g} \\w_o &= 72.3\text{cm}^3 = 72.3\text{g} \\\Delta t &= 0.162^\circ\text{C} \\K_b &= 5.12\text{K}/100\text{g}\end{aligned}$$

$$\Delta t = \frac{K_b \times w_s \times 100}{Mr \times w_o}$$

$$0.162 = \frac{5.12 \times 1.35 \times 100}{Mr \times 72.3}$$

$$Mr = \frac{5.12 \times 1.35 \times 100}{0.162 \times 72.3}$$

$$Mr = 59\text{g mol}^{-1}$$

Hence the molecular weight of solute TB is 59g mol⁻¹.

Qn. 131

The boiling point of benzene is 353.23K. When 1.8g of a non-volatile solute was dissolved in 90g of benzene, the boiling point is raised to 354.11K. Calculate the molar mass of the solute. (K_b for benzene is 2.35K Kg/mol)

Solution

Data

$$\begin{aligned}w_s &= 1.8\text{g} \\w_o &= 90\text{g} \\\Delta t &= (354.11 - 353.23) = 0.88\text{K} \\K_b &= 2.35\text{K Kg/mol}\end{aligned}$$

From,

$$\Delta t = \frac{K_b \times w_s \times 100}{Mr \times w_o}$$

$$Mr = \frac{2.35 \times 1.8 \times 1000}{0.88 \times 90}$$

$$Mr = 53.4\text{g mol}^{-1}$$

Hence the molar mass of the solute is 53.4g mol⁻¹

Qn. 132

Calculate the boiling point and freezing point of solution made by dissolving 2.4g of biphenyl (C₁₂H₁₀) in 75g of benzene. The molar boiling point elevation constant for benzene is 2.53°C/m. The molal freezing point depression constant for benzene is 5.12°C/m. the boiling and freezing point of benzene are 80.1°C and 5.5°C respectively.

Solution

Data

$$\begin{aligned}w_s &= 2.4\text{g} \\w_o &= 75\text{g} \\K_b &= 2.53^\circ\text{C/m} \\K_f &= 5.12^\circ\text{C/m} \\B_p &= 80.1^\circ\text{C} \\F_{pt} &= 5.5^\circ\text{C}\end{aligned}$$

(i) **Required:** Boiling point of the solution

From

$$\Delta t = \frac{K_b \times w_s \times 1000}{Mr \times w_o}$$

$$\Delta t = \frac{2.53 \times 2.4 \times 1000}{154 \times 75}$$

$$\Delta t = 0.526^\circ\text{C}$$

Then

$$\begin{aligned}\text{Boiling point of soln} &= \text{Bpt solvent} + \Delta t \\ &= 80.1^\circ\text{C} + 0.526 \\ &= 80.63^\circ\text{C}\end{aligned}$$

Hence boiling point of solution is 80.63°C or 253.53K .

(ii) Required: Freezing point of solution

From

$$\Delta t = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

$$\Delta t = \frac{5.12 \times 2.4 \times 1000}{154 \times 75}$$

$$\Delta t = 1.06^\circ\text{C}$$

Then freezing point of the solution

$$\begin{aligned}&= F_{\text{pt solvent}} - \Delta t \\ &= 5.5^\circ\text{C} - 1.06 \\ &= 4.44^\circ\text{C}\end{aligned}$$

Then freezing point of the solution is 4.44°C or 277.44K .

Qn. 133

The molar freezing point depression constant of benzene (C_6H_6) is 4.9Kkg/mol selenium exist as a polymer of the type se_x . When 3.26g of selenium is dissolved in 226g of benzene, the observed freezing point is 0.112°C lower than for pure benzene. Deduce the molecular formula of selenium (at mass of $\text{Se} = 78.8\text{g/mol}$).

Solution

$$K_f = 4.89\text{Kkg/mol}$$

$$w_s = 3.26\text{g}$$

$$w_o = 226\text{g}$$

$$\Delta t = 0.112^\circ\text{C}$$

$$At_{\text{Se}} = 78.8\text{g/mol}$$

From,

$$\Delta t = \frac{K_f \times w_s \times 1000}{Mr \times w_o}$$

Make Mr the Subject

$$Mr = \frac{K_f \times w_s \times 1000}{\Delta t \times w_o}$$

$$Mr = \frac{4.9 \times 3.26 \times 1000}{0.112 \times 226}$$

$$Mr = 631\text{g/mol}^{-1}$$

Divide Mr by atomic mass, to get number of atoms in Selenium

$$= \frac{631}{78.8} = 8$$

Then molecular formula of selenium is Se_8

Qn. 134

- (a) Briefly explain the presence of a dissolved solid on a pure solvent in respect of its
- Freezing point
 - Boiling point
- (b) How may the effect in (a) above be used to indicate the purity in organic compounds?

Solution

- (a) (i) The presence of dissolved solid on a pure solvent depress the freezing point of the solution. This means that the freezing point of the pure solvent is higher than that of the solvent which contain dissolved solid.
- (ii) The presence of a dissolved solid on a pure solvent elevate the boiling point of the solution. This means that the boiling point of the pure solvent is lower than that of the solvent which contain dissolved solid.
- (b) Freezing point depression and boiling point elevation can be used to indicate the purity in organic compounds.

- In this case there must be pure control samples of the organic compounds to be determine their purity and whose their freezing point and boiling point are known.